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DOCUMENTATION OF THE NIOSH VALIDATION TESTS

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ABSTRACT

In early 1974 NIOSH and OSHA began a joint program to complete existing environmental exposure standards (29 CFR 1910.1000). This joint program, known as the Standards Completion Program (SCP), required the validation of sampling and analytical methods for each of the chemicals in the regulations. NIOSH conducted the validation portion of the program to provide accurate methods for compliance monitoring by OSHA. This publication provides the detailed information concerning the laboratory evaluations. The evaluation information in 216 individual Backup Data Reports contained here provides detailed information on the laboratory procedure and data from the validation. In addition, an introduction to the program and the statistical protocol used are presented in this documentation.

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The validations were conducted by Stanford Research Institute (SRI) under NIOSH Contract CDC-99-74-45. Arthur D. Little, Inc. and Battelle Columbus Laboratories also performed validations under subcontract to SRI. The authors acknowledge the efforts of the contractors in preparing the material contained in Appendix B.

The selection of methods for validation was based upon the listing in Chapter V of the "OSHA Industrial Hygiene Operations Manual" prepared for OSHA by NIOSH in 1974. J.R. Lynch, J.M. Bryant, J.V. Crable, R.H. Hendricks, R.E. Kupel, F.A. Madsen, and R.J. Freking were responsible for establishing this list of methods.

The statistical protocol for the Standards Completion Program described in Appendix A was developed by Kenneth A. Busch of the Statistical Services Branch, Division of Technical Services, NIOSH. The statistical definitions were prepared by Arthur D. Little, Inc. Their efforts are gratefully acknowledged.

Members of the Measurements Research Branch and the Measurements Support Branch reviewed the individual reports. Their reviews are greatly appreciated.

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INTRODUCTION

Early in 1974 the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) announced a joint program to complete the existing workroom level standards promulgated by the U.S. Department of Labor in 1972 (29 CFR 1910.1000). This Standards Completion Program was completed by NIOSH in September 1976. It involved the development of specialized information from which the employer could determine how to comply with the workplace environmental standards. The informational elements in the proposed standards include: informing the employee of hazards, recordkeeping, defining the necessary personal protective equipment, work practices, engineering controls, and environmental and medical monitoring. No attempt was made to change the present permissible exposure limits to chemical substances. Rather, this joint effort provided detailed information to assist the employer in complying with these exposure standards.

The information developed by NIOSH in the program has been set forth in draft technical standards. These documents were reviewed thoroughly by NIOSH and OSHA personnel. In addition, seven professional societies have reviewed the information prior to its being transmitted to OSHA for consideration in promulgating standards.

This document deals specifically with the means by which NIOSH validated existing sampling and analytical methods for monitoring employee exposure to each substance in the regulations. The data reports contained in Appendix B give detailed technical information which support the validation of 216 sampling and analytical methods in the Standards Completion Program. The actual validations were conducted by Stanford Research Institute (SRI) under Contract CDC-99-74-45 with NIOSH. Arthur D. Little, Inc. and Battelle Columbus Laboratories performed validations for NIOSH under subcontract to SRI. Each contract team set up laboratory facilities and air generation-dilution systems to do complete validations at one-half to two times the OSHA environmental limits shown in 29 CFR 1910.1000, Tables Z-1, Z-2, and Z-3.

The purpose of the validation program is to provide accurate personal sampling and analytical methods in monitoring for non-compliance to the standard by OSHA. The methods are available to others who may want to use them to determine worker exposure to the substances in the OSHA regulations. The validation program was <u>not</u> an attempt to designate the sole procedure by which all worker exposure monitoring must be done. More properly, the validation showed that it is possible

to accurately monitor for the airborne toxic substance. Under the SCP concept, any other analytical methods that an employer may use to measure employee exposure must meet the accuracy requirements set forth in the proposed standard.

Unlike the U.S. Environmental Protection Agency which has a Reference Method for air monitoring, the SCP draft technical standards uniformly designate certain accuracy requirements which must be met for any methods not validated by NIOSH, but are used by an employer for environmental monitoring. There is a sliding scale of proposed requirements depending upon the concentration of the substance. Above the permissible exposure level, the method must come within ±25% of the "true" concentration at the 95% confidence level. Above the action level, i.e., one-half the OSHA standard, and up to and including the permissible exposure level, the method must measure within ±35% of the "true" concentration. At or below the action level, the method must come within ±50% of the "true" concentration. These accuracy requirements refer to the (net) error of the sampling and analytical method used by an employer to measure employee exposure. Should the employer choose to use the NIOSH validated method, the SCP program assures that the method can meet these accuracy requirements.

In conclusion, the technical information presented in this report supports the validation of 216 sampling and analytical methods by NIOSH. An introduction to the Standards Completion Program, a summary of the validation criteria, and the statistical protocol are included. Each of the validated methods is available in the second edition of the "NIOSH Manual of Analytical Methods." In addition, the Sampling Data Sheets (SDS) are available in the "NIOSH Manual of Sampling Data Sheets." The SDS is designed for technical personnel who collect the samples in the field. NIOSH hopes that this information not only supports the completion of the OSHA standards and assists OSHA in its compliance program, but in addition, makes available to the public methods which have received a critical evaluation in the laboratory.

EXPERIMENTAL PROTOCOL

The timing and magnitude of the Standards Completion Program did not allow for collaborative testing of the sampling and analytical methods since approximately 400 methods were scheduled to be validated in a two-year period. Nevertheless, it was deemed important to test both the sampling and the analytical portions of the method. The validation program was designed to evaluate these two parts of the method. Each of the two-part validations was carried out in a single laboratory and although many of the methods have been used in the field previously, no field validations were undertaken.

Initially, the analytical method was tested to assure that it was acceptable for analyte recovery as well as for precision. The sampling medium was spiked with known amounts of the test chemical at three levels corresponding to one-half, one, and two times the occupational standard for a given air volume. The success of this portion of the validation assured that the analytical precision was acceptable for the desired concentration range. In addition, the analytical bias and recovery of the substance from the sampling medium was determined in these spiking tests. At least 90% of the material should be removed from a membrane filter and measured. For the solid sorbent sampling methods such as the charcoal tube, a minimum desorption efficiency of 75% was necessary for validation. For some of the substances a five-day storage test was performed to determine sample stability.

The second portion of the validation was to test the efficiency of the sampling procedure. This required the generation of known air concentrations of the toxic substance in a laboratory generator-dilution system. Three concentrations at one-half, one, and two times the environmental standard were prepared to test the sampling method. Where possible, the generated concentrations were verified by a completely independent sampling and analytical method. For some substances this procedure was not possible and calculations based upon known flow and delivery rates, or on the experimentally determined collection efficiency, sample stability, and recovery were necessary to estimate the generated concentration. After selecting the recommended flow rate and sample volume, the samples were collected from the laboratory generation-dilution system. Six samples at each of the three concentrations were collected for the overall method validation. These 18 samples as well as the 18 spiked sample results obtained in the analytical validation were used to form the basic statistical set of data. The data were then used to determine the precision, bias and accuracy of the method.

The NIOSH criterion for a valid method was based upon whether the method results can come within $\pm$25% of the "true" value. This accuracy requirement applies to the range 0.5 to 2.0 times the environmental standard and is given at the 95% confidence level.

In order to meet this basic criterion NIOSH established several requirements which are noted below.

1. The accuracy criterion applies to the overall sampling and analytical method.
2. A personal sampling method must be used.
3. For time-weighted average (TWA) environmental limits, the minimum sampling period is one hour for individual samples. Several samples may have to be taken to determine the 8-hour TWA.

4. The sample must be stable for at least five days so that samples can be shipped to a central laboratory for analysis. This requirement was added after the program began and is reflected in the individual backup data reports in Appendix B.

5. During testing an unexplained bias of no more than about 10% is acceptable. The bias is defined as the difference between the concentration in the generator as determined by the independent method and the concentration as determined by the method being tested.

6. For solid sorbent sampling, the desorption efficiency must be at least 75%.

In addition, a statistical protocol was initially developed to deal with the precision errors evaluated in the laboratory testing program. The details of the entire statistical protocol are contained in Appendix A. Further development of the statistical protocol dealt with combinations of precision and bias to determine whether the method met the NIOSH accuracy criterion for validation. There were two purposes for the statistical protocol. First, the level of accuracy stated in the NIOSH draft technical standards from the Standards Completion Program is required to be met at the 95% confidence limit. The statistical protocol provides methods of data analysis which translate this standard into statistical parameters which can be estimated from the data and tested for statistical significance. Second, the efficient design of the laboratory study required a statistical component in order to minimize the number of samples taken and thus the overall cost of the testing.

Figure 1 shows the relationship between bias and the method precision as determined in the laboratory. The bias is estimated from the difference between the generated concentration and the concentration as determined by the test method. The acceptable region is indicated by the shaded area. Note that when the bias is zero, the largest acceptable true CV_T is 0.128 but the largest acceptable estimated CV_T is 0.105. More measurements are required to narrow the gap between these two values and still provide 95% confidence that the accuracy standard had been met. As the bias increases, the method must have a lower CV_T in order for it to come within $\pm$25% of the true value on the average 95% of the time.

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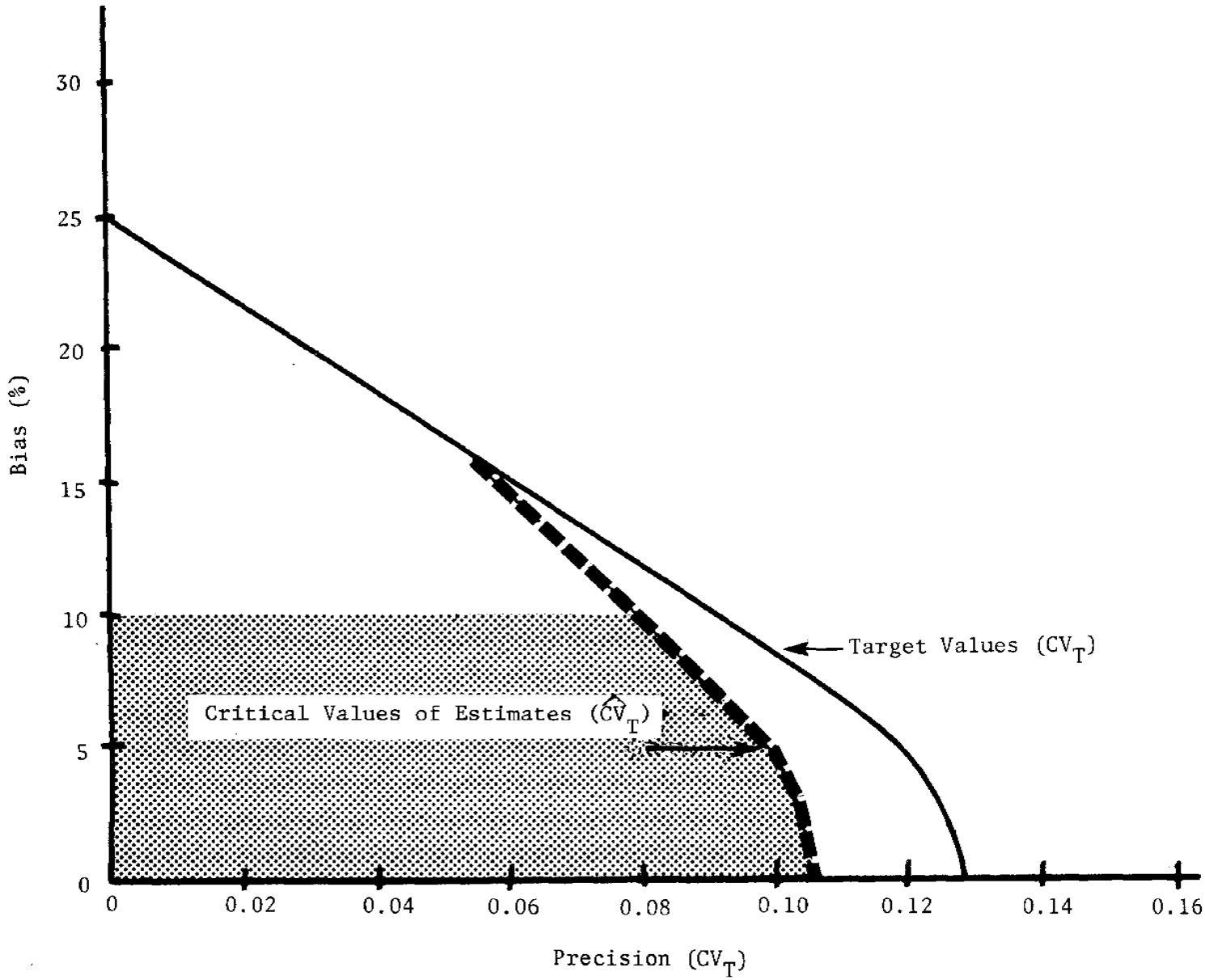

Figure 1. Combinations of CV_T and bias which yield net errors (sampling and analysis) of 25% or less at least 95% of the time.

DATA PRESENTATION

The laboratory procedures and data used to validate each of the 216 methods are presented in Backup Data Reports (BUD). These reports form the bulk of this document. The BUD's are ordered by an S-number which is identical to the number assigned to the associated Sampling Data Sheet and Sampling and Analytical Method validated in the study.

The information in the BUD includes the procedure validated; any modifications to the original method given by NIOSH; the generation procedure; appropriate breakthrough capacity, collection efficiency or stability testing data; a precision and accuracy discussion; the actual data for the spiked analysis samples and the generated samples; and references.

Each analysis table indicates the results of the spiking test in which known amounts of the analyte are added to the sampling media at one-half (0.5S), one (1S), and two (2S) times the OSHA environmental standard for the recommended sample volume. The precision results for the analytical portion of the method are also presented.

Each sampling and analysis table shows the results of the laboratory generated samples collected at the three test concentration levels. Where direct measurement of the generated concentration by an independent method was possible, the "Taken" value is shown and an overall recovery or bias is calculated. Where no direct measurement was possible, other information such as sample stability and collection efficiency were necessary to determine if any bias existed. In some of the BUD's, specialized tables and other necessary information are presented to support the validated method.

APPENDIX A. SCP Statistical Protocol
Prepared by
Kenneth A. Busch

INTRODUCTION

This Appendix gives the steps of a recommended statistical protocol for analysis of air concentration data for hazardous chemicals. The purpose of the statistical analysis is to estimate the total precision error of a subject method and resolve this error into its components due to the sampling method (less pump error), the analytical method (including error in the desorption efficiency factor), and an assumed level of pump error.

MAXIMUM NET ERROR FOR UNBIASED METHOD

The present suggested standard for air monitoring accuracy is that the absolute total error (sampling plus analysis) should be less than 25% in at least 95% of samples analyzed at the level of the standard. In the case of normally distributed sampling and analysis errors (and no bias) the above requirement implies that the true coefficient of variation of the total error, denoted by CV_T, should be no greater than 0.128 derived as follows: $CV_T = 0.25/1.96 = 0.128$. The number 0.128 is the largest true precision for a net error of $\pm$ 25% at the 95% confidence level. The number 1.96 is the appropriate t-statistic from the t-distribution at the same confidence level.

However, the estimated values of CV_T (denoted by $\widehat{CV}_T$), which are reported by SRI under the NIOSH contract CDC-99-74-45, will themselves be subject to appreciable random errors of estimation. Therefore, the "critical value" not to be exceeded by an experimental value of $\widehat{CV}_T$ must be lower than the maximum permissible true value of CV_T which is implied by the wording of the accuracy standard. The maximum permissible true value of CV_T will be referred to as its "target level" and the required degree of confidence that a subject method meets this accuracy standard can be obtained by calculating an appropriate [$(1 - \alpha)$ probability level] upper confidence limit on $\widehat{CV}_T$ and obeying the following decision rule:

> Rule: Reject the method if the 95% upper confidence limit on $\widehat{CV}_T$ exceeds the target level of CV_T. Otherwise, accept the method.

As would be expected, in order to be able to have the 95% degree of confidence that $\widehat{CV}_T$ does not exceed its target level, we must also suffer the penalty of sometimes falsely rejecting "good" methods whose true CV_T is satisfactory, but for which the $\widehat{CV}_T$ estimate is not precise enough to keep its upper confidence limit below the target value. Such decision errors, referred to as "type-1 errors," will occur

randomly but with a controlled frequency of less than 5% of cases. The 5% probability of type-1 error is by definition the complement of the confidence level.

As an example, consider a $\widehat{CV}_T$ which is a pooled value determined from three groups of six samples. The $\widehat{CV}_T$ would have to be less than 0.105 in order for us to be 95% confident that the true $CV_T \leq 0.128$ (i.e., in order for us to be 95% confident that future errors by the same method would not exceed $\pm$ 25% more than 5% of the time). The critical value of $\widehat{CV}_T$ is 0.105 at the $\alpha = 0.05$ type-1 error level. Thus, for an unbiased method the largest laboratory determined CV_T should not exceed 0.105.

To be reasonably sure that a test method meets the NIOSH accuracy standard, we have adopted the following decision rule: if the estimate ($\widehat{CV}_T$) is below 10.5%, the 95% upper confidence limit on CV_T would be below 12.8% and the method would be found satisfactory. This decision rule is based on assumptions that errors are normally distributed and the method is unbiased. Figure 1 (see text) provides adjustments to the critical values of $\widehat{CV}_T$ when a method is biased. The dotted curve gives critical values of $\widehat{CV}_T$ as a function of bias for a statistical significance test performed at the 5% type-I error level (i.e., 95% confidence level).

It is important to note that the critical values of $\widehat{CV}_T$ for Figure 1 were computed under the assumption that the bias is a known quantity. This was necessary because the protocol contains no standard statistical experimental design for determination of bias by means of an independent method. In cases where confidence limits can be calculated for the bias, the critical $\widehat{CV}_T$ should be read from the dotted curve at a position corresponding to the 95% upper confidence limit for the bias. This is a conservative procedure but better critical values could only be determined if the standard error of the bias were known.

The calculated points through which the curves of Figure 1 were drawn using a French curve are given below.

Bias	Target CV_T	Critical $\widehat{CV}_T$
0%	12.8%	10.5%
2.5%	12.5%	10.3%
5.0%	11.8%	9.8%
10.0%	9.1%	7.9%
15.0%	6.1%	5.8%
16.8%	5.0%	5.0%
20.0%	3.0%	(Unattainable)
25.0%	0%	(Unattainable)

8<

Due to the fact that CV_P, the coefficient of variation of pump error, is assumed to be 5%, any method with a bias above 16.8% could not meet the accuracy standard (no matter how small were the CV_S and CV_A for other sampling errors and analysis errors, respectively).

DEFINITIONS AND SYMBOLS

Mean - arithmetic mean or average ($\bar{x}$), defined as the sum of the observations divided by the number of observations (n).

Standard deviation - The positive square root of the variance which is defined as the sum of squares of the deviations of the observations from their mean ($\bar{x}$) divided by one less than the number of observations (n - 1).

$$\text{std dev} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

CV - coefficient of variation or relative standard deviation, defined as the standard deviation divided by the mean.

$$CV = \frac{\text{std dev}}{\text{mean}}$$

CV_1 - coefficient of variation (estimated value) for the six analytical samples at each of the 0.5, 1, and 2X OSHA standard level.

CV_2 - coefficient of variation (estimated value) for the six generated samples at each of the 0.5, 1, and 2X OSHA standard level.

$\overline{CV}$ - pooled coefficient of variation, in this program, the value derived from the coefficients of variation (of a given type e.g., CV_1 or CV_2) obtained from the analysis of 6 samples at each of the three test levels - 0.5, 1 and 2X OSHA standard level. The mathematical equation is expressed as:

$$\overline{CV} = \sqrt{\frac{\sum_{i=1}^{3} f_i (CV_i)^2}{f}}$$

where: f_i = degrees of freedom, equal to number of observations (n) minus one, at the i^{th} level.

CV_i = coefficient of variation (CV_1 or CV_2) of the observations at the i^{th} concentration level.

$f = \sum_{i=1}^{3} f_i$

i = Index for the 3 concentration levels.

$\overline{CV}_1$ - pooled coefficient of variation calculated as above based on data for the 18 analytical (spiked) samples (3 groups of 6).

$\overline{CV}_{A+\overline{DE}}$ - derived correction to include precision error due to the use of the desorption efficiency factor, which is an average of 6 values.

$$\overline{CV}_{A+\overline{DE}} = \overline{CV}_1\sqrt{7/6} = 1.0801\ \overline{CV}_1$$

$\overline{CV}_{A+\overline{AMR}}$ correction factor analogous to the desorption efficiency factor noted above except that this notation is used where the factor is associated with analytical method recovery (AMR) other than for solid sorbents.

$$\overline{CV}_{A+\overline{AMR}} = 1.0801\ \overline{CV}_1$$

$\overline{CV}_2$ - pooled coefficient of variation based on the data for the 18 generated samples.

$\overline{CV}_S$ - coefficient of variation of the sample collection, not including the variability of the personal sampling pump. The value dependent on the data from the 18 analytical and 18 generated samples.

$$\overline{CV}_S = \sqrt{(\overline{CV}_2)^2 - (\overline{CV}_1)^2}$$ (See "Note" below)

CV_P - coefficient of variation due to the pump error, assumed to be equal to 0.05.

$\overline{CV}_T$ - coefficient of variation of total procedure which consists of the composite variations in sampling and analysis, desorption efficiency, and the pump error.

$$\overline{CV}_T = \sqrt{(\overline{CV}_S)^2 + (\overline{CV}_{A+DE})^2 + (\overline{CV}_P)^2}$$

or:

$$\overline{CV}_T = \sqrt{(\overline{CV}_2)^2 - (\overline{CV}_1)^2 + 1.1667\ (\overline{CV}_1)^2 + (0.05)^2}$$

or:

$$\overline{CV}_T = \sqrt{(\overline{CV}_2)^2 + 0.1667\ \overline{CV}_1^{\,2} + (0.05)^2}$$ (See "Note" below)

Note: In case $\overline{CV}_2 < \overline{CV}_1$, take $\overline{CV}_S = 0$. Then replace $\overline{CV}$ by a pooled estimate $(\overline{CV}_1{}^*)$ based on $\overline{CV}_1$ and $\overline{CV}_2$, namely

$$\overline{CV}_1^{\,*} = \sqrt{\frac{f_1\,\overline{CV}_1^{\,2} + f_2\,\overline{CV}_2^{\,2}}{f_1 + f_2}}$$

where f_1 and f_2 are the respective f-values used in the denominators of $\overline{CV}_1^{\,2}$ and $\overline{CV}_2^{\,2}$.

GRUBB'S TEST for rejection of an observation is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

$$B_1' = \frac{x - \bar{x}}{s} \quad \text{or} \quad \left(\frac{\bar{x} - x}{s}\right)$$

where:

x = observation being tested (most distant from the mean)
$\bar{x}$ = mean of n observations
s - standard deviation based on n-1 degrees of freedom

For any 6 observations, a value can be rejected if $B_1' \geq 2.130$. The B_1' limit is based on a 1% significance level (i.e., a B_1' value calculated from the data can be expected to exceed 2.13 only 1% of the time if the observation is a legitimate one conforming to the underlying theory).

BARTLETT'S TEST for homogeneity of CVs is applied in order to test the feasibility of "pooling the Coefficients of Variation" for any set of 18 generated samples (i.e., 6 at each of the 0.5, 1, and 2X OSHA standard level). The following equation for Chi-squared, with 2 degrees of freedom, was used:

$$\text{Chi squared} = \frac{f \ \ln \ (\overline{CV}_2)^2 - \sum_{i=1}^{3} f_i \ \ln \ (\overline{CV}_{2i})^2}{1 + \frac{1}{3\ (3-1)}\left[\left(\sum_{i=1}^{3} \frac{1}{f_i}\right) \frac{1}{f}\right]}$$

where:

$\overline{CV}_2$ = pooled coefficient of variation of 18 generated samples

$\overline{CV}_{2i}$ = coefficient of variation of 6 generated samples at the i^{th} level

f_i = degrees of freedom associated with $(CV_{2i})^2$ and equal to number of observations at the i^{th} level minus one.

$f = \sum_{i=1}^{3} f_i$

In order to pass Bartlett's test at the 1% significance level, Chi-squared must be less than or equal to 9.21 (Chi-squared has 2 degrees of freedom).

APPENDIX B. SCP Backup Data Reports

The following 216 Backup Data Reports are arranged and numbered to correspond to the S-number assigned to the sampling and analytical method and sampling data sheet. These numbers were assigned at the beginning of the Standards Completion Program. The missing numbers were assigned to methods which failed the validation. The Backup Data Reports are cross-referenced by chemical name in the Index.

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Backup Data Report

Substance:	Acetone
OSHA Standard:	2380 mg/cu m
Chemical used for validation	Acetone, Mallinckrodt A.R.

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of acetone in air is described in NIOSH Method S1, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 0.7, 1.5, and 3 times the OSHA standard by the method described in S1. Samples of acetone in air were generated by the procedure described in Reference No. 1. These samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 15 minutes at a rate of approximately 0.13 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of acetone in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 15 minutes). The "true" value for the concentration of acetone generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for acetone.

Breakthrough Tests

An experiment was done to test the breakthrough of the front section of the charcoal tubes. Breakthrough time is defined as the time at which the effluent concentration from the tube reaches 5% of the influent concentration. Individual tests were done on each of 6 charcoal tubes containing 100 mg of Lot 105 charcoal. The individual breakthrough times were 17, 24, 23, 24, 23, and 21 minutes when a generated atmosphere of 4300 mg/cu m of acetone was sampled at a rate of **0.195 liter per minute.**

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in Method S1. Results are given in the laboratory data section of this report.

Reference

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

Note: In Section 4 of Method S1, Acetone, an average of the values obtained from Tests 1 and 4 was used to obtain the relative standard deviation in Section 4.1 and the "accuracy" figure in Section 4.2. This was done because several problems were encountered with the other two tests due to start-up difficulties and it is believed that Tests 1 and 4 better represent the precision and accuracy of the method. (The CV_T was calculated using data from all the experiments listed under Laboratory Results.)

Laboratory Results
Acetone

Analytical - Desorption Efficiencies (D.E.)*

Test 1			Test 2			Test 3			Test 4		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
2.36	1.90	0.805	3.55	2.95	0.831	7.11	6.01	0.845	14.2	13.3	0.937
2.36	1.91	0.809	3.55	2.97	0.837	7.11	6.38	0.897	14.2	13.5	0.951
2.36	1.92	0.814	3.55	3.00	0.845	7.11	5.98	0.841	14.2	13.4	0.944
2.36	1.93	0.818	3.55	2.94	0.828	7.11	6.37	0.896	14.2	12.6	0.887
2.36	1.87	0.792	3.55	2.96	0.834	7.11	6.50	0.914	14.2	13.4	0.944
2.36	1.84	0.780	3.55	3.05	0.859	7.11	6.40	0.900	14.2	13.1	0.922
Mean**		0.803			0.839			0.882			0.931
S***		0.014			0.011			0.031			0.024

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found	Taken	Found
1200	1180	1550	1720	3060	3580	4530	4380
1200	1280	1550	1630	3060	3430	4530	4020
1200	1240	1550	1640	3060	3440	4530	4400
1200	1280	1550	1410	3060	3120	4530	4330
1200	1200	1550	1640	3060	3600	4530	4410
1200	1230	1550	1720	3060	3720	4530	3940
Mean**	1230		1630		3480		4250
S***	41		114		208		210
Error (%)****	+2.5		+5.2		+14		-6.2

*D.E. = $\frac{\text{mg found}}{\text{mg taken}}$

**Mean = $\frac{\Sigma \text{ D.E.}}{n}$

***S = Standard Deviation

****Error (%) = $\frac{\text{Found - Taken}}{\text{Taken}}$ X 100

Acetone

Statistical Analysis

Regression Equations

Analysis

$$Y = 1.079 - 0.03396X_{1i} - 0.04628X_{2i}$$

t-values : -0.01948 -0.01987

Sampling and Analysis

$$Y = 1.861 - 800.6X_{1i} - 0.00016X_{2i}$$

t-values : -4.35 -4.75

Coefficients of Variation:

$CV_1^2 = 0.00057$ Analysis

$CV_2^2 = 0.00431$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.082$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

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Backup Data Report

Substance:	2-Butanone
OSHA Standard:	590 mg/cu m
Chemical used for validation:	2-Butanone, Mallinckrodt A.R.

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 2-butanone in air is described in NIOSH Method S3, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by the method described in S3. Samples of 2-butanone in air were generated by the procedure described in Reference No. 1. These samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 50 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of 2-butanone in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 50 minutes). The "true" value for the concentration of 2-butanone generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for 2-butanone.

Breakthrough Tests

The breakthrough time was determined at a vapor concentration equal to twice the OSHA standard level. It is defined as the time at which the effluent concentration from the first (100 mg) section of the charcoal tube reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube during collection of a field sample.

To measure the breakthrough time, 6 tubes containing the first (100 mg) section of charcoal were tested in parallel. The tubes were placed in the sample generation apparatus. The test atmosphere was pulled through each tube at an average flow of 172 ml/minute, using

0.006 inch diameter orifices to regulate the flow. The orifices were connected to a manifold, which was evacuated to about 22 inches Hg using a metal bellows pump. This pump was selected because it does not leak and is constructed entirely of stainless steel; therefore it will not alter the composition of the test atmosphere. The effluent from the pump was then sampled using a gas chromatograph equipped with a gas sampling valve. The elution time was adjusted so that injections could be made every 4 minutes. Peak height measurements were used to determine the concentration of 2-butanone in the pump effluent.

The data are plotted in Figure 1. Breakthrough occurred at 86 minutes and the total volume sampled was 15 liters. The data fell on a smooth curve with no apparent discontinuities. If channeling had occurred in one or more tubes, sharp rises in effluent concentration, followed by an apparent leveling off, should be observed early in the run. For instance, if one tube channeled, the effluent concentration should rise sharply to about 16.7% of the concentration in the test atmosphere, but, since the flow through each tube is regulated separately, it should not rise appreciably above 17% until breakthrough occurred in the other tubes. If channeling had occurred, it would have been necessary to repeat the experiment with a second set of tubes.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in Method S3. Results are given in the laboratory data section of this report.

Reference

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

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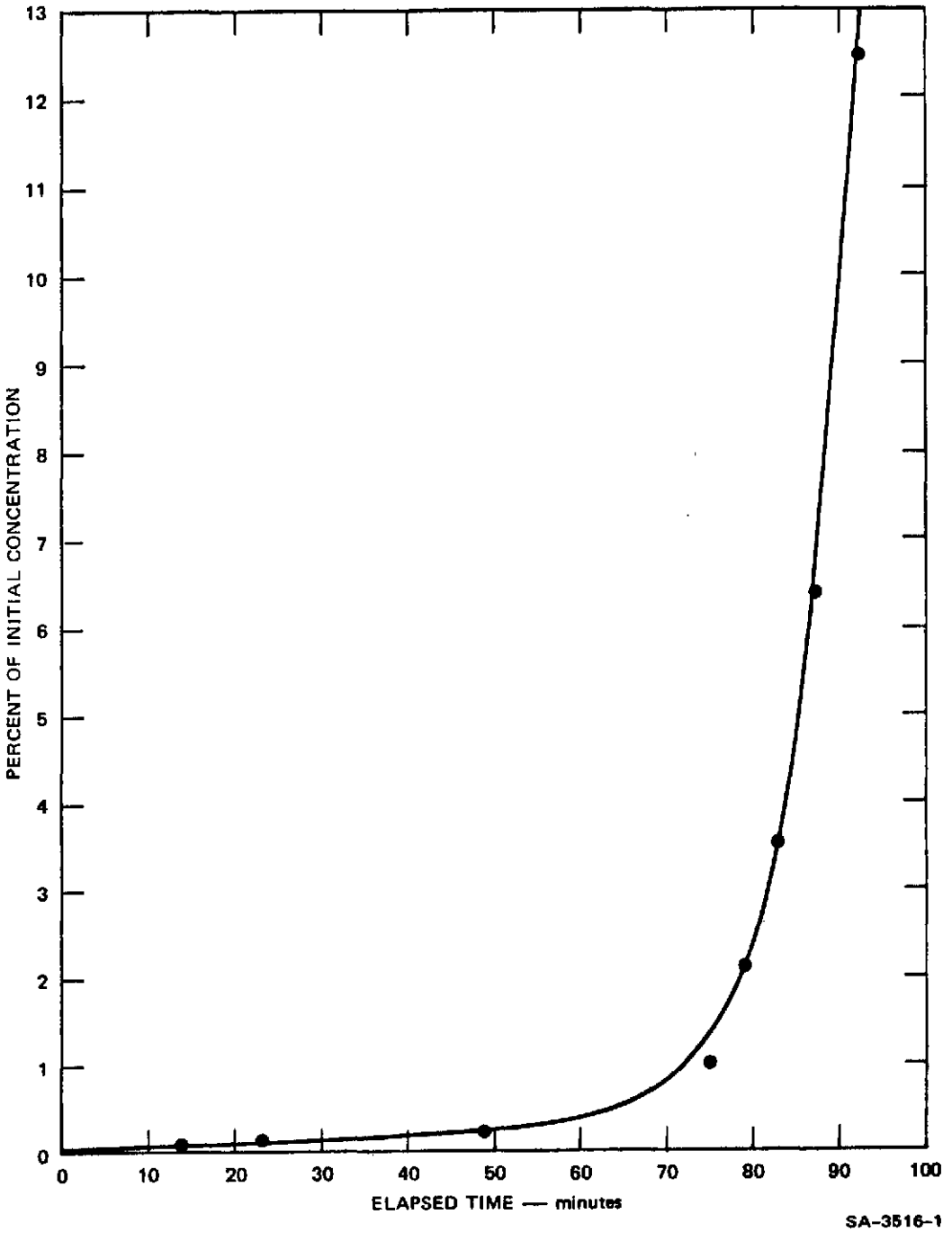

FIGURE 1 2-BUTANONE BREAKTHROUGH

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Laboratory Results

2-Butanone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
2.49	2.05	0.823	4.97	4.34	0.873	10.0	8.46	0.846
2.49	1.89	0.759	4.97	4.17	0.839	10.0	8.76	0.876
2.49	1.92	0.771	4.97	4.25	0.855	10.0	8.91	0.891
2.49	1.86	0.747	4.97	4.15	0.835	10.0	8.68	0.868
2.49	1.78	0.715	4.97	4.20	0.845	10.0	8.50	0.850
2.49	1.74	0.699	4.97	4.13	0.831	10.0	8.85	0.885
Mean**		0.752			0.846			0.869
S***		0.044			0.016			0.018

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
382	359	764	832	1240	1390
382	399	764	833	1240	1340
382	397	764	835	1240	1260
382	374	764	751	1240	1290
382	390	764	849	1240	1420
382	360	764	895	1240	1340
Mean**	380		833		1340
S***	18		46		60
Error (%)****	-0.52		+9.0		+8.1

*D.E. = mg found/mg taken

**Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation

****Error (%) = 100 (Found - Taken)/Taken

2-Butanone

Statistical Analysis

Regression Equations

Analysis:

$$Y = 1.000 + 0.00033X_{1i} + 0.0000\,X_{2i}$$

t-values : +0.00007 0.0000

Sampling and Analysis

$$Y = 1.34 - 112.7X_{1i} - 0.00014X_{2i}$$

t-values : -2.16 -1.20

Coefficients of Variation:

$CV_1^2 = 0.00140$ Analysis

$CV_2^2 = 0.00275$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.072$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance:	Hydrogen Sulfide, No. S4
OSHA Standard:	20 ppm (30 mg/cu m) - Ceiling 50 ppm (70 mg/cu m) - Peak
Chemical used for validation:	Hydrogen Sulfide in Nitrogen Linde Specialty Gas

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of hydrogen sulfide in air is described in NIOSH Method S4, which has been adapted from P&CAM 126. The primary standard was $Na_2S \cdot 9H_2O$ which was weighed out and made up to volume in water. Its concentration was verified by iodometric titration. This standard was used to prepare spiked samples to obtain a standard curve.

Generated hydrogen sulfide in air at 0.5X, 1X, and 2X the OSHA standard was collected by aspirating a measured volume of air through cadmium hydroxide in water. The sulfide was precipitated as cadmium sulfide, and the collected sulfide was determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with an acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride.

Modifications

Several modifications to Method No. P&CAM 126 were made.

It was necessary to modify P&CAM 126 to accomodate the higher concentration of hydrogen sulfide in the sample. This method was intended for the range of 1.1-100 µg/cu m, and the OSHA standard is 30 mg/cu m. The analytical method as changed is essentially the same except for the change in the range of the standard curve. The amounts of reagents used in the color-producing reaction are increased, and the final volume increased to 250 ml. It was found that the absorbance curve became non-linear at higher concentrations of sulfide.

The sampling rate was changed from 1 liter per minute to 0.20 liter per minute to collect an amount of hydrogen sulfide in 10 minutes at the OSHA standard that would be suitable for analysis.

The method of preparing the absorbing solution was altered (as described in Section 7.8 of NIOSH Method No. S4 for Hydrogen Sulfide), but the amount of absorbing solution used was unchanged.

Method No. P&CAM 126 suggested the use of permeation tubes as a source of hydrogen sulfide to test sampling efficiency. The concentrations required necessitated using a source capable of emitting a much higher level than is available from a permeation tube. A cylinder of hydrogen sulfide in dry nitrogen was used.

Generation

A cylinder of nitrogen containing a concentration of 98 mg/cu m hydrogen sulfide was used. To obtain concentrations of hydrogen sulfide in air at 0.5X, 1X, and 2X the OSHA standard, an apparatus consisting of pressure regulators, needle valves, and flow meters for the nitrogen and dry air diluent stream was used.

Flow of hydrogen sulfide in nitrogen was controlled by a needle valve and a previously calibrated flow meter with a range of 0.2 to 2 liters per minute. Diluent dry air from a cylinder was controlled by a similar needle valve-flow meter combination in the range of 1 to 20 liters per minute. The hydrogen sulfide in nitrogen and the diluent air were combined in a mixing chamber at atmospheric pressure, from which they flow through a baffle tube, in which mixing takes place and then into a 1 liter sampling flask, which is provided with several nipples from which samples can be taken. Sampling was done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate. Samples were collected for 10 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate.)

In order to calculate the concentration of hydrogen sulfide in the chamber from which sampling was conducted, it was first determined that the concentration of hydrogen sulfide in the cylinder was 98 mg/cu m. Previously calibrated flow meters and critical orifices were used to set the flow of hydrogen sulfide and of dry air for dilution into the sampling chamber. The calculation was done with the formula given below:

$$C = \frac{cf}{F + f}$$

where:

C = concentration of hydrogen sulfide in mg/cu m

c = concentration of hydrogen sulfide in nitrogen, before dilution

F = flow of diluent air, as measured by calibrated flow meter

f = flow of hydrogen sulfide in nitrogen, as measured by calibrated flow meter.

Data for the three concentrations are as follows:

Test No.	c (mg/cu m)	f (liter/minute)	F (liter/minute)	C (mg/cu m)
1	98	0.23	2.41	8.5
2	98	0.23	0.88	20.0
3	98	0.23	0.13	63.0

Precision and Accuracy

The statistical procedures used are described in Reference No. 1.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

Laboratory Results

Analytical Method (values in μg H_2S)

0.5 OS		1.0 OS		2.0 OS	
Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
31	31	62	61	124	124
31	31	62	65	124	125
31	30	62	59	124	125
31	30	62	60	124	127
31	32	62	65	124	129
31	31	62	63	124	126
*Mean	31.0		62.0		126.0
**S	0.7		2.6		1.8
***Recovery	100%		100%		102%

Sampling and Analysis (mg/cu m)

Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
8.5	9.2	20	20	63	67
8.5	10.0	20	22	63	60
8.5	8.8	20	25	63	57
8.5	6.8	20	21	63	62
8.5	7.4	20	23	63	66
8.5	9.8	20	21	63	68
*Mean	8.7		22.0		63.0
**S	1.3		1.8		4.7
***Recovery	102%		110%		100%

$$*\text{Mean} = \frac{\Sigma \text{ Obs.}}{n}$$

**S = Standard Deviation

$$***\text{Recovery} = \frac{\text{Mean of Observed Value}}{\text{Calculated Value}} \times 100$$

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 0.180 + 0.00020\ X_{1i} - 0.111\ X_{2i}$$

t values : 0.426 0.061

Sampling and Analysis

$$Y = 1.26 - 1.81\ X_{1i} - 0.00364\ X_{2i}$$

t values : -1.44 -1.61

Coefficients of Variation:

$CV_1^2 = 0.00084$ analysis

$CV_2^2 = 0.0121$ sampling and analysis

$CV_P^2 = 0.0025$ pump error

$CV_T = 0.121$

where:

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: Manganese and Compounds (as Mn), No. S5

OSHA Standard: 5 mg/cu m (ceiling)

Chemical used for validation: Manganese Sulfate ($MnSO_4 \cdot H_2O$), Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S5 which has been adapted from P&CAM 173. Type AA Millipore Filters, 37 mm, were spiked with solutions of manganese sulfate monohydrate, digested and diluted to 100 ml for analysis. Details of the analytical procedure may be found in NIOSH Method No. S5. A Perkin-Elmer Model 503 Atomic Absorption Spectrometer was used for the analysis.

Validity of the digestion procedure for the most probable industrial forms of manganese - the oxides - was determined as follows:

Approximately 1 mg samples of MnO_2 and Mn_3O_4 were fired at 900°C for 15 - 18 hours and then digested for analysis using the recommended procedure. The following results were obtained:

	Expected (mg)	Found (mg)	%
MnO_2	1.14	1.13	99.2
	0.98	1.03	105
Mn_3O_4	1.33	1.26	94.8

thus assuring that the general procedure should be valid for most samples to be encountered.

Modification

There were no modifications of P&CAM 173.

Generation

Simulated air samples were generated from nebulized solutions of manganous sulfate using an ERC Collison type generator. The total air flow of about 75 ℓpm was split between the six simultaneous 37 mm filter samples collected at 1.5 ℓpm and a large 142 mm reference filter operating at about 65 ℓpm. The large filter served as the "true" or known value with which to reference the 37 mm samples. Samples were collected for 15 minutes, since the standard for manganese is a ceiling value.

The particulate apparatus was calibrated using a sodium chloride aerosol, and concentrations determined at each of the sample locations with a sodium flame photometer. The details of the generation equipment and calibration modes employed are described in the Antimony S2 Backup Data Report.

Variation in aerosol concentration at each location was as follows:

Location		Na level
142 mm filter		100 (reference point)
37 mm location	1	103
	2	103
	3	103
	4	103
	5	100
	6	103

Sample collection was controlled by critical flow orifices with the following flow rates under the sampling conditions:

Sample Orifice	Flow rate (NTP) ℓpm
1	1.36
2	1.32
3	1.73
4	1.74
5	1.74
6	1.37

Collection Efficiency

The collection efficiency of the MCEF Type AA filter is greater than 99%.

Precision and Accuracy

Statistical data were obtained by using the recommended BMDO3R program. The data are summarized in the attached tables.

Experimental Results

Analytical Method (values in total µg)

0.5 OS*		1.0 OS		2.0 OS	
Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
62.5	62	125	121	250	251
62.5	62	125	121	250	251
62.5	62	125	121	250	251
62.5	62	125	121	250	251
62.5	62	125	122	250	251
62.5	61	125	122	250	251
Mean	61.8		121.3		251
S**	0.9		0.7		0.0
Accuracy (%)	99		97		100

Sampling and Analysis (mg/m^3)

Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
2.96	3.09	6.10	5.49	11.23	10.04
2.96	2.89	6.10	5.33	11.23	9.89
2.96	3.05	6.10	6.14	11.23	9.90
2.96	3.03	6.10	5.42	11.23	10.11
2.87	2.61	5.92	5.27	10.90	9.74
2.96	3.01	6.10	5.59	11.23	9.91
2.945		6.07		11.18	
Mean	2.94		5.54		9.93
S	0.18		0.32		0.13
Accuracy (%)	100		91		89

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* OSHA standard

** $S = (\Sigma d^2/n-1)^{1/2}$

Statistical Analysis

Regression Equations

Analysis

$$Y = 0.867 + 5.889X_1 + 0.00046X_2$$

Sampling and Analysis

$$Y = 0.811 + 0.529X_1 + 0.00265X_2$$

Coefficients of Variation

$$\widehat{CV}_1 = CV_A = 0.0046$$

$$\widehat{CV}_2 = CV_S = 0.0412$$

$$\widehat{CV}_3 = CV_T = 0.065$$

where CV_S excludes the pump error ($CV_P = 0.05$) and

$$CV_T = (CV_S^2 + CV_P^2)^{\frac{1}{2}}$$

or

$$\widehat{CV}_3 = (CV_2^2 + 0.05^2)^{\frac{1}{2}}$$

BACKUP DATA REPORT

Substance: Ozone, No. S8

OSHA Standard: 0.1 ppm (0.2 mg/cu m)

Ozonized air was generated by "corona discharge" employing a Purification Sciences Inc. (psi) ozone generator. The ozone was added to a 610 cu ft smog chamber where the concentration was continuously monitored by a REM Model 612 Atmospheric Ozone Monitor. The principle of operation of the REM is based on the chemiluminescent reactions of ozone with ethylene gas. When the desired ozone concentration was attained (approximately 0.4 mg/cu m), six samples were collected in alkaline potassium iodide (KI) solution, and two in neutral KI. The samples were collected simultaneously, via Teflon® manifold, to obtain groups of samples at the same concentration. Subsequent sets of ozone samples at lower concentrations were obtained by diluting the chamber to the desired level with purified air and repeating the sampling procedure.

The neutral KI samples were analyzed immediately and served as the independent method of measuring on the ozone concentration. The alkaline KI samples were capped and stored in the dark for three to seven days prior to analysis.

It was necessary to modify certain procedures in the recommended alkaline method. The sampling period specified (100 minutes) would have exceeded the capacity of the alkaline KI solution at the 0.4 mg/cu m level. The recommended time is 45 minutes at 1.0 liters per minute. However, at the 0.1 mg/cu m level a sampling period of 1-1/2 hours will give better accuracy. The acidification procedure specified did not permit vigorous enough stirring to expel all of the CO_2 absorbed by the alkaline KI solution. It is recommended that acidification be carried out directly in the impinger, without transferring, where thorough mixing can be achieved without loss of solution.

The reaction of ozone with alkaline KI is not quantitative and is concentration dependent. Therefore a conversion equation must be used to convert readings to values equivalent to the neutral KI method. This equation, given on the statistical analysis page, was derived by using the coefficients obtained by performing a multiple regression analysis of alkaline KI values versus the neutral values. The results are based on the premise that the neutral KI values are the best values that can be obtained.

Laboratory Results
Ozone

Sampling and Analysis (Values in mg/cu m)

Actual*	Found**	Actual	Found
0.065	0.068 (0.029)	0.074	0.068 (0.029)
0.065	0.073 (0.033)	0.074	0.068 (0.029)
0.065	0.071 (0.032)	0.074	0.066 (0.027)
0.065	0.069 (0.031)	0.074	0.067 (0.028)
0.065	0.069 (0.031)	0.074	0.068 (0.029)
0.065	0.071 (0.032)		
Mean***	0.070		0.067
S****	0.002		0.0009
Recovery*****	108%		91%

Actual	Found	Actual	Found	Actual	Found
0.139	0.132 (0.090)	0.263	0.267 (0.221)	0.412	0.406 (0.356)
0.139	0.146 (0.104)	0.263	0.267 (0.221)	0.412	0.410 (0.360)
0.139	0.138 (0.088)	0.263	0.266 (0.220)	0.412	0.425 (0.374)
0.139	0.130 (0.110)	0.263	0.264 (0.218)	0.412	0.414 (0.363)
0.139	0.130 (0.084)	0.263	0.249 (0.203)	0.412	0.405 (0.355)
0.139	0.137 (0.095)				
Mean	0.136		0.263		0.412
S	0.0138		0.0077		0.0081
Recovery	98%		100%		100%

*Determined by neutral-buffered KI method (average of two values).

**Values in parentheses are the readings before NEUTRAL/ALKALINE correction.

***$\text{Mean} = \frac{\Sigma \text{ Values}}{n}$

****S = Standard Deviation.

*****$\text{Recovery} = \frac{\text{Found Value}}{\text{Actual Value}} \times 100\%$.

Statistical Analysis
Ozone

Regression Equations

Analysis (apply to corrected values)

$$Y = -0.028 + 0.8365\ X + 0.290033\ X^2$$

where Y = amount found

X = amount present

Correction Equation (to correct alkaline KI values for concentration dependent stoichiometry variations

$$Y = 0.038 + 1.038\ X - 0.010505\ X^2$$

where Y = neutral KI equivalent value

X = value found by alkaline KI method

Coefficients of Variation

CV_2 = 0.0633 (Sampling and Analysis)

CV_T = 0.0806 (total including 5% rotameter error)

BACKUP DATA REPORT

Substance: Camphor, No. S10

OSHA Standard: 12.5 mg/cu m

Chemical used for validation: Refined Camphor (Nippon Camphor Company, Ltd.)

The procedure followed for validation of the method is essentially that of P&CAM 127, with the exception that an internal standard has been added for improved accuracy.

For determination of desorption efficiency 100 mg samples of charcoal* were placed in 2 ml Hewlett Packard Automatic Sample Injector vials and spiked with an 6.23 percent solution of camphor in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for the 0.5, 1, and 2 times the OSHA standard levels. Preliminary experiments indicate that desorption with carbon disulfide containing 1 percent methanol gave significantly greater desorption efficiency than carbon disulfide alone, so the mixed solvent was used for the quantitative studies. Carbon disulfide alone gave desorption efficiencies of 0.74, 0.75, and 0.77 at loadings equivalent to 0.5, 1, and 2 times the OSHA standard level. The details of the analytical procedures are given in the Analytical Procedures section of this report.

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of this report. The total gas flow rate of the first stage was 22.4 liters per minute. Since Camphor is a solid, it was injected as a 30 percent solution in n-heptane; the injection rate was 0.12 ml/hr or 0.036 g camphor/hr. Sampling time was 100 minutes at a nominal flow rate of 200 ml/min for each tube.

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level. Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices.

*SKC, lot 105.

The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours there was no detectable change in the effluent concentration. Thus the capacity of this lot of charcoal exceeds 1 mg of camphor and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Laboratory Results
Camphor

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS				1.0 OS				2.0 OS			
Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg
0.125	0.125	0.997	0.124	0.249	0.245	0.983	0.254	0.498	0.405	0.934	0.486
0.125	0.122	0.973	0.121	0.249	0.236	0.955	0.247	0.498	0.481	0.966	0.503
0.125	0.130	1.038	0.130	0.249	0.238	0.957	0.248	0.498	0.484	0.971	0.505
0.125	0.124	0.992	0.124	0.249	0.240	0.965	0.250	0.498	0.485	0.973	0.507
0.125	0.126	1.006	0.125	0.249	0.241	0.970	0.251	0.498	0.471	0.947	0.493
0.125	0.125	0.002	0.125	0.249	0.239	0.960	0.248	0.498	0.470	0.943	0.491
Mean***		1.001	0.125			0.965	0.250			0.956	0.498
S****		0.0214	0.0029			0.0104	0.0028			0.0166	0.0085

S10-3

Sampling and Analysis

Analysis, mg		mg/cu m		Analysis, mg		mg/cu m		Analysis, mg		mg/cu m	
Found	Corr.	Taken	Found	Found	Corr.	Taken	Found	Found	Corr.	Taken	Found
0.090	0.090	5.69	4.71	0.221	0.229	12.52	12.81	0.541	0.564	26.79	28.62
0.104	0.104	5.69	5.48	0.245	0.255	12.52	12.54	0.502	0.524	26.79	29.61
0.102	0.102	5.69	5.53	0.243	0.253	12.52	12.69	0.494	0.516	26.79	27.90
0.103	0.103	5.69	5.43	0.223	0.231	12.52	12.76	0.466	0.488	26.79	26.51
0.096	0.096	5.69	6.05	0.222	0.231	12.52	12.39	0.532	0.555	26.79	30.66
0.102	0.102	5.69	5.47	0.093	0.090	12.52	*****	0.526	0.549	26.79	28.43
Mean			5.45				12.63				28.62
S			0.41				0.21				1.42
Recovery******			96%				101%				107%

* DE = $\frac{\text{mg found}}{\text{mg added}}$

** Corr. = mg found ÷ D.E.

*** Mean = $\frac{\Sigma \text{ values}}{n}$

**** S = Standard Deviation

***** Value deleted because of suspected leak

****** Recovery = $\frac{\text{mg found}}{\text{mg taken}}$ X 100%

Statistical Analysis
Camphor

Regression Equations

Analysis

$$Y = -0.002 + 1.018\ X\ -0.0301\ X^2$$

where Y = amount found, corrected for desorption efficiency (mg)

and X = amount added

Sampling and Analysis

$$Y = -0.69 + 1.039 + 0.00206\ X^2$$

where Y = amount found (mg/cu m)

and X = amount taken

Coefficients of Variation

CV_1 = 0.0179 (Analysis)

CV_2 = 0.0542 (Sampling + Analysis)

CV_T = 0.0737 (Total*)

*Including pump error of 0.05

Analytical Procedures

Because of the large number of determinations involved in this program, use of an automatic sample injector was considered highly advantageous. Since the use of internal standards in gas chromatographic analyses is widely used to increase the reliability of quantitative data obtained the internal standard technique was used throughout this work.

Equipment Used

For this work a Varian Model 1860 Gas Chromatograph equipped with a Hewlett-Packard Automatic Sample Injector was used. The automatic sample injector has a programming option that flushes the syringe with solvent immediately after the sample is injected. This prevents possible deposition of components in the syringe and minimizes contamination of subsequent samples. (The standard model--and most, if not all, other automatic sample injectors flush the syringe just before a new sample is injected.)

Peak area measurements were made with an Infotronics CRS204 Digital Integrator. The integrator was connected in such a manner that it was reset and started by a signal from the automatic sample injector so that automatic overnight operation was possible.

The reproducibility of sample injection by the automatic injection system used was checked by making 12 replicate injections of a carbon disulfide solution containing 1 mg/ml of n-tridecane and 2-heptanone. The CV of the absolute peak areas was 3.5 percent and the CV of the area ratios was 0.38 percent. The room temperature was maintained at 68-72 F to minimize evaporation of the carbon disulfide.

Calibration

For analysis by the internal standard method a known amount of an internal standard is added to each sample. The amount of the sample present is determined by referring to a calibration curve which is a plot of $\frac{\text{peak area of sample}}{\text{peak area of int std}}$ versus amount of sample. The calibration curve is determined experimentally by analyzing a series of known solutions in which the concentration of internal standard is kept constant and the concentration of sample is varied by known amounts. Although the flame ionization detector response is linear over a wide range of concentrations under ideal conditions, which would give a linear calibration curve, there is frequently an appreciable deviation from linearity, especially at the higher concentrations.

In this work, calibration curves were prepared by making solutions of the compound under study in CS_2 at 4 or 5 concentrations including those expected when the compound is collected at 0.5, 1.0, and 2.0 times the

standard concentration. A normal hydrocarbon internal standard was used at a concentration equivalent to 1.0 times the standard concentration.

Gas chromatographic determination of areas for the compound and internal standard were then made (duplicate samples with duplicate injections for each sample).

The calibration curves were constructed analytically (rather than graphically), using a gradratic least squares program (written in FORTRAN). The program fits all data points to the quadratic formula, (1).

$$y = ax + bx^2 \qquad (1)$$

In the general case a third coefficient would be used, the y intercept value, but in this case, the y intercept must be zero if the gas chromatograph and integrator is functioning properly.

For each chromatogram the area ratio, $\frac{\text{peak area of sample}}{\text{peak area of int std}}$, was determined and the replicate determination for each solution were averaged. Input to the program was then pairs of data, concentration of sample and area ratio. In a first mode of operation, (Mode 1) the program computes the best fit of the points to the formula (1), and outputs the coefficients a and b. The least squares coefficients were recorded for use in calculating the results of subsequent analyses.

In a second mode of operation, (Mode 2) the program uses the coefficients to calculate the value of y corresponding to values of x which are input to the program. This is equivalent to the graphical procedure of determining the y value corresponding to the specific value of x from a plot of x versus y.

Analysis of Samples

The solutions for analysis, containing the internal standard were chromatographed in duplicate or triplicate under the conditions used for determination of the calibration curve. For each solution the peak area ratios of the replicates were averaged. The average value was then used as input to the quadratic least squares program in Mode 2 to determine the amount of samples found.

Determination of Desorption Efficiency

For determination of desorption efficiency, 100 mg of activated charcoal was put in a 2-ml vial used with the automatic sample injector. The calculated amount of the compound being studied was deposited directly with a 10 µl syringe. The vial was then sealed with an aluminum cap containing a Teflon-lined rubber septum and allowed to stand overnight. For liquid samples the neat liquid was injected directly if the amount required

was 2 µl or more. When smaller amounts of liquids were required and in the case of all solids, the compound was dissolved in sufficient solvent so that at least 2 µl of solution was added. This was done because dispensing less than 2 µl would lead to too great an error in the amount actually deposited on the charcoal.

After standing overnight to ensure complete absorption, 1.00 ml of solvent containing internal standard was injected directly into the capped vial. After a minimum of 30 minutes with occasional shaking to achieve equilibration the vial was placed in the sample tray of the automatic sample injector for gas chromatographic analysis. Use of the capped vials for automatic sample injector directly eliminated the transfer from a separate extraction tube thus gave a procedure that is essentially the same as that of the recommended standard method.

Six samples were run at each concentration and two replicate injections were made from each sample. The amount of material in solution (i.e., desorbed) was determined by the procedure described in the previous section on "analyses of samples". The values from the replicate injections of each sample were averaged, and using the quadratic least squares program described above, a desorption curve was constructed analytically. The coefficient's output was recorded for use in determining the correction factor to be used in subsequent analysis of samples eluted from charcoal traps. In this case the curve was not forced through the origin, i.e., the equation (2) was used.

$$y = a + bx + cx^2 \qquad (2)$$

Analysis of Charcoal Trap Samples

For samples adsorbed on charcoal, the main section and the backup section were placed in separate sample injector vials. To each vial was added 1 ml of solvent containing the internal standard. After a minimum of 30 minutes with occasional shaking to achieve the equilibration, the vials were placed in the sample tray of the automatic sample injector for gas chromatographic analysis. As in the case of calibration and desorption efficiency runs two replicate injections were made on each sample. The results for the replicates for each sample were averaged, and the amount of material found was determined by using this value as input to the quadratic least squares program using the coefficients for the calibration curve. As before, this process is the analytic equivalent of reading the amount found from a calibration plot. Similarly, correction for desorption efficiency was made by employing the same program and the coefficients from the desorption efficiency determination.

Atmosphere Generation System

The test atmosphere generation and sample collection system used was designed and built specially for this program. For volatile materials which exist as a vapor, a syringe pump was used to meter the substance to be vaporized. Successive dilution was used so that concentrations 0.5, 1, and 2 times the OSHA standard were generated and sampled simultaneously.

System Description

The analyte was metered into a 10-mm glass tube by a syringe pump and a gas-tight syringe. The pump was calibrated prior to use. In addition, the delivery was checked by weighing the syringe before and after the run. The tube was heated by a heating tape to about 25 C below the boiling point of the material. The analyte was vaporized in a stream of nitrogen gas (nitrogen was used to avoid oxidation). Nitrogen (and input air) flows were controlled by flowmeters. The nitrogen stream was then mixed with dry air. At this point the total flow was ~12 liters per minute. The mixture then entered a vertical manifold constructed of 25-mm O.D. glass tubing. The manifold was 4-ft long with three dilution stages, spaced ~1 foot apart. At each stage, the stream was diluted with an additional 12 liters per minute of dry air. The dilution air was dispersed through a gas dispersion tube in the middle of the tube. The annular clearance was such that the Reynold's number was 2320, assuring complete mixing. Four inches below the air inlet 12 liters per minute was taken from the center of the manifold for sample collection, leaving 12 liters per minute to move down the manifold to the next dilution stage. The concentrations at the three stages were 2, 1, and 0.5 times the OSHA standard respectively. A F.I.D. continuous monitor was used to determine that the concentration was constant; 300 ml/min was taken for the continuous monitor at the bottom of the manifold, and the balance of the sample stream was vented.

At each stage, 8 charcoal tubes were connected to a single glass manifold. This provided 2 spares in case one or two tubes were broken. The charcoal tubes were connected to the glass manifold by polypropylene connectors. Each was followed by a separate critical flow orifice. The vacuum sides of the critical flow orifices were manifolded together with rubber tubing.

For 200 ml/min collections, the 8 tubes had a combined flow of 1.6 liters per minute, so a 10.4-liters-per-minute auxiliary orifice was used to keep the total flow at 12 liters per minute.

A separate 12 liters per minute orifice on the exit tube at each stage was used for bypass during startup and shutdown. Flow through either the manifold or bypass was controlled by solenoid valves which apply vacuum to the bypass orifices for startup and shutdown, or through the manifold orifices for sample collection.

System Operation

This system was used for both breakthrough determination and sample collections.

A carbon-vane centrifugal pump was used to pump the effluent air through a hydrogen flame analyzer to confirm that this concentration remained constant during a run. Actual concentrations were calculated from the delivery rate of the analyte and the gas flow rates.

For breakthrough determination, a valve permitted pumping the effluent from the 8 charcoal tubes on the manifold through the analyzer; this allowed determination of the concentration of the effluent from the charcoal tubes as a percentage of the influent concentration. This did not give separate breakthrough values for each tube, but if one tube broke through prematurely there would be a discontinuity in the curve. Only the first stage (2 times the OSHA standard) was used for breakthrough.

For sample collection and analysis all three stages are sampled simultaneously.

BACKUP DATA REPORT

Substance: Mesityl Oxide, No. S12

OSHA Standard: 100 mg/cu m

Chemical used for validation: 4-Methyl-3-penten-2-one, 99% (Chemical Samples Company)

The procedure followed for validation of the method is essentially that of P&CAM 127, with the exception that an internal standard has been added for improved accuracy.

For determination of desorption efficiency 100 mg samples of charcoal* were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and spiked with an 8 percent solution of mesityl oxide in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for the 0.5, 1, and 2 times the OSHA standard levels. Preliminary experiments indicate that desorption with carbon disulfide containing 1 percent methanol gave significantly greater desorption efficiency than carbon disulfide alone, so the mixed solvent was used for the quantitative studies. Carbon disulfide alone gave desorption efficiencies of 0.645, 0.695, and 0.729 at loadings equivalent to 0.5, 1, and 2 times the OSHA standard level. The details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 1. The total gas flow rate of the first stage was 22.4 liters per minute, and the rate of mesityl oxide injection was 0.282 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level. Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration was

*SKC, lot 105.

below 0.25 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 9.6 mg of mesityl acid and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirements.

Reference

1. Backup Data Report for Camphor, No. S10.

Laboratory Results
Mesityl Oxide

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS				1.0 OS				2.0 OS			
Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg
0.500	0.390	0.780	0.501	1.000	0.815	0.815	1.011	2.000	1.666	0.833	2.004
0.500	0.396	0.792	0.518	1.000	0.795	0.795	0.988	2.000	1.671	0.836	2.010
0.500	0.378	0.757	0.487	1.000	0.812	0.812	1.007	2.000	1.684	0.842	2.024
0.500	0.386	0.772	0.496	1.000	0.813	0.813	1.008	2.000	1.666	0.833	2.004
0.500	0.388	0.775	0.498	1.000	0.795	0.795	0.987	2.000	1.608	0.804	1.937
0.500	0.395	0.790	0.507	1.000	0.816	0.816	1.012	2.000	1.674	0.837	2.013
Mean***		0.778	0.499			0.808	1.002			0.831	1.999
S****		.0128	.0078			.0098	.0117			.0135	.0310

Sampling and Analysis

Analysis, mg		mg/cu m		Analysis, mg		mg/cu m		Analysis, mg		mg/cu m	
Found	Corr.	Taken	Found	Found	Corr.	Taken	Found	Found	Corr.	Taken	Found
0.378	0.487	44.6	52.1	0.773	0.965	98.0	107.8	1.948	2.347	209.8	238.3
0.387	0.498	44.6	52.4	0.855	1.064	98.0	104.8	1.652	2.005	209.8	226.5
0.367	0.473	44.6	51.4	0.896	1.113	98.0	111.8	1.656	2.010	209.8	217.3
0.371	0.479	44.6	50.4	0.771	0.963	98.0	106.4	1.719	2.083	209.8	226.4
0.343	0.460	44.6	51.9	0.812	1.011	98.0	108.7	1.686	2.044	209.8	225.9
0.372	0.479	44.6	51.5	0.647	0.813	98.0	89.8	1.804	2.181	209.8	226.0
Mean			51.6				104.9				226.7
S			0.7				7.8				6.7
Recovery			116%				107%				108%

* DE = $\frac{\text{mg found}}{\text{mg added}}$ ***Mean = $\frac{\Sigma \text{ values}}{n}$ *****Recovery = $\frac{\text{mg found}}{\text{mg taken}}$ X 100%

** Corr. = mg found ÷ D.E. ****S = Standard Deviation

Statistical Analysis
Mesityl Oxide

Regression Equations

Analysis

$$Y = -0.0068 + 1.0152\ X\ -0.00622\ X^2$$

where Y = amount found, corrected for desorption efficiency (mg)

and X = amount added

Sampling and Analysis

$$Y = 9.69 + 0.915\ X + 0.00057\ X^2$$

where Y = amount found (mg/cu m)

and X = amount taken

Coefficients of Variation

CV_1	=	0.0143	(Analysis)
CV_2	=	0.0502	(Sampling + Analysis)
CV_T	=	0.0708	(Total*)

*Including pump error of 0.05.

BACKUP DATA REPORT

Substance: 5-Methyl-3-heptanone*, No. S13

OSHA Standard: 130 mg/cu m

Chemical used for validation: 5-Methyl-3-heptanone (Chemical Samples Company)

The procedure followed for validation of the method is essentially that of P&CAM 127, with the exception that an internal standard has been added for improved accuracy.

For determination of desorption efficiency 100 mg samples of charcoal** were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and spiked with a 10.4 percent solution of 5-methyl-3-heptanone in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for the 0.5, 1, and 2 times the OSHA standard levels. Preliminary experiments indicate that desorption with carbon disulfide containing 1 percent methanol gave significantly greater desorption efficiency than carbon disulfide alone, so the mixed solvent was used for the quantitative studies. Carbon disulfide alone gave desorption efficiencies of 0.795, 0.807, and 0.816 at loadings equivalent to 0.5, 1, and 2 times the OSHA standard level. The details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 1. The total gas flow rate of the first stage was 22.4 liters per minute, and the rate of 5-methyl-3-heptanone injection was 0.365 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level. Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes** containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 3 hours the effluent concentration had

*Listed incorrectly as Ethyl sec-amyl ketone in 29 CFR 1610.93.
**SKC, lot 105.

reached only 1.25 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 9 mg of 5-methyl-3-heptanone and at the recommended sampling rate, the breakthrough volume is greater than 36 liters. This meets the above requirement.

Reference

1. Backup Data Report for Camphor, No. S10.

Laboratory Results
5-Methyl-3-Heptanone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS				1.0 OS				2.0 OS			
Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg
0.650	0.565	0.869	0.620	1.300	1.156	0.889	1.297	2.600	2.307	0.887	2.591
0.650	0.607	0.933	0.669	1.300	1.131	0.870	1.269	2.600	2.278	0.876	2.559
0.650	0.607	0.933	0.669	1.300	1.189	0.915	1.335	2.600	2.360	0.908	2.649
0.650	0.599	0.922	0.660	1.300	1.144	0.880	1.283	2.600	2.328	0.895	2.614
0.650	0.568	0.873	0.624	1.300	1.149	0.884	1.289	2.600	2.324	0.894	2.610
0.650	0.611	0.924	0.662	1.300	1.187	0.913	1.332	2.600	2.287	0.880	2.569
Mean***		0.909	0.650			0.892	1.301			0.890	2.599
S****		.0299	.0223			.0182	.0268			.0115	.0332

Sampling and Analysis

Analysis, mg		mg/cu m		Analysis, mg		mg/cu m		Analysis, mg		mg/cu m	
Found	Corr.	Taken	Found	Found	Corr.	Taken	Found	Found	Corr.	Taken	Found
0.566	0.622	57.5	66.5	1.210	1.358	126.0	151.8	2.862	3.204	272.0	325.2
0.443	0.480	57.5	50.5	1.231	1.382	126.0	136.2	2.511	2.817	272.0	318.3
0.541	0.593	57.5	64.5	1.489	1.675	126.0	168.3	2.376	2.668	272.0	288.4
0.567	0.623	57.5	65.6	1.100	1.234	126.0	136.3	2.602	2.917	272.0	317.1
0.527	0.586	57.5	66.2	1.151	1.291	126.0	138.8	2.640	2.959	272.0	327.0
0.545	0.597	57.5	64.2	1.125	1.261	126.0	139.4	2.554	2.865	272.0	296.9
Mean			62.9				145.1				312.1
S			6.2				12.8				15.8
Recovery			109%				115%				115%

* DE = $\frac{\text{mg found}}{\text{mg added}}$

** Corr. = mg found ÷ D.E.

*** Mean = $\frac{\Sigma \text{ values}}{n}$

****S = Standard Deviation

*****Recovery = $\frac{\text{mg found}}{\text{mg taken}}$ X 100%

Statistical Analysis
5-Methyl-3-Heptanone

Regression Equations

Analysis

$$Y = -0.00063 + 1.0024\ X - 0.00100\ X^2$$

where Y = amount found, corrected for desorption efficiency (mg)

and X = amount added

Sampling and Analysis

$$Y = 7.99 + 1.248\ X + 0.00026\ X^2$$

where Y = amount found (mg/cu m)

and X = amount taken

Coefficients of Variation

CV_1 = 0.0243 (Analysis)

CV_2 = 0.0915 (Sampling + Analysis)

CV_T = 0.1043 (Total*)

*Including pump error of 0.05

BACKUP DATA REPORT

Substance:	Methyl n-Amyl Ketone, No. S15
OSHA Standard:	465 mg/cu m
Chemical used for validation:	2-Heptanone, 99% (Chemical Samples Company)

The procedure followed for validation of the method is essentially that of P&CAM 127, with the exception that an internal standard has been added for improved accuracy.

For determination of desorption efficiency 100 mg samples of charcoal* were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and spiked with neat 2-heptanone injected with a 10-µl microliter syringe at 0.5, 1, and 2 times the OSHA standard levels. Carbon disulfide was used as the desorbing solvent. The details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 1. The total gas flow rate of the first stage was 22.4 liters per minute, and the rate of methyl n-amyl ketone injection was 1.25 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level. Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough After 3 hours the effluent concentration had reached only 3.4 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 15 mg of methyl n-amyl ketone and at the recommended sampling rate, the breakthrough volume is greater than 36 liters. This meets the above requirements.

Reference

1. Backup Data Report for Camphor, No. S10.

*SKC, lot 105.

Laboratory Results
Methyl n-Amyl Ketone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS				1.0 OS				2.0 OS			
Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg
2.320	1.804	0.777	2.302	4.650	3.792	0.815	4.659	9.300	7.891	0.849	9.177
2.320	1.798	0.775	2.296	4.650	3.766	0.810	4.629	9.300	7.824	0.841	9.107
2.320	1.818	0.783	2.319	4.650	3.849	0.828	4.726	9.300	7.974	0.857	9.264
2.320	1.823	0.786	2.326	4.650	3.831	0.824	4.704	9.300	7.984	0.858	9.274
2.320	1.829	0.788	2.333	4.650	3.766	0.810	4.629	9.300	8.158	0.877	9.455
2.320	1.811	0.780	2.311	4.650	3.767	0.810	4.630	9.300	8.181	0.880	9.480
Mean***		0.782	2.314			0.816	4.663			0.860	9.293
S****		0.0050	0.0141			0.0079	.426			0.0153	0.148

S15-2

Sampling and Analysis

Analysis, mg		mg/cu m		Analysis, mg		mg/cu m		Analysis, mg		mg/cu m	
Found	Corr.	Taken	Found	Found	Corr.	Taken	Found	Found	Corr.	Taken	Found
0.888	1.181	197	*****	3.350	4.145	433	463	8.266	9.567	925	971
1.614	2.072	197	218	3.419	4.226	433	416	7.663	8.938	925	1010
1.516	1.953	197	212	3.538	4.364	433	439	7.487	8.751	925	946
1.547	1.990	197	209	3.148	3.907	433	432	6.622	7.827	925	851
1.468	1.909	197	216	3.312	4.100	433	441	7.661	8.936	925	987
1.571	2.019	197	217	3.274	4.056	433	448	7.784	9.065	925	939
Mean			214				440				951
S			10.7				15.7				55.5
Recovery******			109%				102%				103%

* De = $\frac{\text{mg found}}{\text{mg added}}$

** Corr. = mg found ÷ D.E.

*** Mean = $\frac{\Sigma \text{ values}}{n}$

**** S = Standard Deviation

***** Value deleted because of suspected leak

****** Recovery = $\frac{\text{mg found}}{\text{mg taken}}$ X 100%

Statistical Analysis
Methyl n-Amyl Ketone

Regression Equations

Analysis

$$Y = -0.0423 + 1.0199\ X\ -0.00173\ X^2$$

where Y = amount found, corrected for desorption efficiency (mg)

and X = amount added

Sampling and Analysis

$$Y = 36.47 + 0.883\ X + 0.00011\ X^2$$

where Y = amount found (mg/cu m)

and X = amount taken

Coefficients of Variation

CV_1	=	0.0112	(Analysis)
CV_2	=	0.0434	(Sampling + Analysis)
CV_T	=	0.0662	(Total*)

*Including pump error of 0.05

BACKUP DATA REPORT

Substance:	Ethyl Butyl Ketone, No. S16 (3-Heptanone)
OSHA Standard:	230 mg/cu m
Chemical used for validation:	3-Heptanone, 99% (Chemical Samples Company)

The procedure followed for validation of the method is essentially that of P&CAM 127, with the exception that an internal standard has been added for improved accuracy.

For determination of desorption efficiency 100 mg samples of charcoal* were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and spiked with an 18.4 percent solution of 3-heptanone in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for the 0.5, 1, and 2 times the OSHA standard levels. Preliminary experiments indicate that desorption with carbon disulfide containing 1 percent methanol gave significantly greater desorption efficiency than carbon disulfide alone, so the mixed solvent was used for the quantitative studies. Carbon disulfide alone gave desorption efficiencies of 0.783, 0.795, and 0.803 at loadings equivalent to 0.5, 1, and 2 times the OSHA standard level. The details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 1. The total gas flow rate of the first stage was 22.4 liters per minute, and the rate of 3-heptanone injection was 0.622 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level. Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 2 hours the effluent concentration had

*SKC, lot 105.

reached only 1 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 11 mg of 3-heptanone and at the recommended sampling rate, the breakthrough volume is greater than 24 liters. This meets the above requirements.

Reference

1. Backup Data Report for Camphor, No. S10.

Laboratory Results
Ethyl Butyl Ketone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS				1.0 OS				2.0 OS			
Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg	Added mg	Found mg	D.E.	Corr.** mg
1.150	1.066	0.927	1.147	2.300	2.204	0.958	2.362	4.600	4.319	0.939	4.569
1.150	1.076	0.936	1.158	2.300	2.147	0.933	2.302	4.600	4.409	0.959	4.662
1.150	1.117	0.971	1.202	2.300	2.160	0.939	2.317	4.600	4.446	0.966	4.699
1.150	1.012	0.880	1.089	2.300	2.134	0.928	2.289	4.600	4.283	0.931	4.532
1.150	1.068	0.929	1.150	2.300	2.134	0.928	2.289	4.600	4.268	0.928	4.517
1.150	1.067	0.927	1.148	2.300	2.112	0.918	2.265	4.600	4.350	0.946	4.601
Mean***		0.928	1.149			0.934	2.304			0.945	4.597
S****		.0291	.0361			.0136	.0332			.0153	.0721

Sampling and Analysis

Analysis, mg		mg/cu m		Analysis, mg		mg/cu m		Analysis, mg		mg/cu m	
Found	Corr.	Taken	Found	Found	Corr.	Taken	Found	Found	Corr.	Taken	Found
0.779	0.838	98.3	89.2	1.977	2.122	216.3	237.1	4.124	4.369	462.8	443.5
0.796	0.856	98.3	90.1	1.801	1.935	216.3	190.6	3.629	3.857	462.8	435.8
0.739	0.795	98.3	86.4	1.755	1.885	216.3	189.5	3.588	3.814	462.8	412.4
0.817	0.879	98.3	92.5	1.608	1.729	216.3	191.	3.593	3.819	462.8	415.1
0.722	0.776	98.3	87.7	1.123	1.209	216.3	*****	3.624	3.852	462.8	425.6
0.757	0.814	98.3	87.5	2.018	2.166	216.3	239.3	2.385	2.554	462.8	*****
Mean			89.0				209.5				426.5
S			2.2				26.2				13.3
Recovery			91%				97%				92%

* DE = $\frac{\text{mg found}}{\text{mg added}}$

** Corr = mg found ÷ D.E.

*** = $\frac{\Sigma \text{ values}}{n}$

****S = Standard Deviation

*****Values deleted because of suspected leaks

******Recovery = $\frac{\text{mg found}}{\text{mg taken}}$ X 100%

Statistical Analysis
Ethyl Butyl Ketone

Regression Equations

Analysis

$$Y = -0.01150 + 1.0117\ X\ -0.02159\ X^2$$

where Y = amount found, corrected for desorption efficiency (mg)

and X = amount added

Sampling and Analysis

$$Y = -19.70 + 1.144\ X\ -0.00039\ X^2$$

where Y = amount found (mg/cu m)

and X = amount taken

Coefficients of Variation

CV_1	=	0.0219	(Analysis)
CV_2	=	0.0705	(Sampling + Analysis)
CV_T	=	0.0864	(Total*)

*Including pump error of 0.05

Backup Data Report

Substance:	Hexone, No. S18 (Methyl Isobutyl Ketone)
OSHA Standard:	409 mg/cu m
Chemical used for validation:	Methyl Isobutyl Ketone, Mallinckrodt Analytical Reagent

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of hexone in air is described in NIOSH Method S18, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S18. Samples of hexone in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 52.6 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of hexone in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate rate for that sample X 52.6 minutes). The "true" value for the concentration of hexone generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for hexone.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference No. 2) Breakthrough occurred in 91.7 minutes when a concentration of 1145 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S18, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

Hexone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
2.070	1.801	0.870	4.14	3.75	0.905	8.28	7.78	0.939
2.070	1.816	0.878	4.14	3.66	0.885	8.28	7.76	0.938
2.070	1.787	0.863	4.14	3.69	0.892	8.28	7.73	0.934
2.070	1.836	0.887	4.14	3.75	0.906	8.28	7.76	0.938
2.070	1.819	0.879	4.14	3.74	0.904	8.28	7.76	0.938
2.070	1.839	0.888	4.14	3.78	0.910	8.28	7.72	0.933
Mean**		0.878			0.900			0.937
S***		0.010			0.010			0.002

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
208	196.4	413	411	836	817
208	202.5	413	408	836	833
208	181.8	413	376	836	825
208	176.5	413	400	836	839
208	199.5	413	391	836	813
208	200.9	413	371	836	795
Mean**	192.9		393		820
S***	11.0		16.6		15.7
Error (%)****	-7.2		-4.8		-1.9

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

Hexone

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 0.875 - 0.02922\ X_{1i} + 0.00775\ X_{2i}$$

t-values: -0.817 3.71

Sampling and Analysis:

$$Y = 0.940 - 5.03\ X_{1i} + 0.00006\ X_{2i}$$

t-values -0.2993 0.586

Coefficients of Variation:

$CV_1^2 = 0.00007$ Analysis

$CV_2^2 = 0.00159$ Sampling and Analysis

$CV_P = 0.0025$ Pump Error

$CV_T = 0.0640$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: Cyclohexanone, No. S19

OSHA Standard: 200 mg/cu m

Chemical used for validation: Cyclohexanone, Baker A.R.

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of cyclohexanone in air is described in NIOSH Method S19, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S19. Samples of cyclohexanone in dry air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1), and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 40 minutes at a rate of approx. 1 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of cyclohexanone in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 40 minutes). The "true" value for the concentration of cyclohexanone generated was determined by comparison with a "bag" standard as described in Reference No. 1, using a total hydrocarbon analyzer for measurement.

Modification of P&CAM 127

This method worked satisfactorily for cyclohexanone at the sample sizes generated using a 40 liter sample. Tests for desorption were first conducted using amounts of cyclohexanone equivalent to a 7.5 liter sample at 0.5X, 1X and 2X the OSHA standard and desorption efficiencies did not meet the 0.75 criterion specified by the Project Officer for this amount of analyte. The following solvents were tried for desorption:

Solvent	Amount	Approx. D.E. at 1X Standard
Carbon disulfide	0.5 ml	0.5
1% Methanol in carbon disulfide	0.5 ml	0.5
5% Methanol in carbon disulfide	0.5 ml	0.5
Methylene chloride	1.0 ml	0.25
2% Methanol in methylene chloride	1.0 ml	0.25

Methanol and ethanol were eliminated as possible desorbents since they interferred with gas chromatography of cyclohexanone.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2.) Breakthrough occurred in 69 minutes when a concentration f 392 mg/cu m was sampled at a rate of 0.94 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

Cyclohexanone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
3.764	2.894	0.769	7.53	6.02	0.800	18.82	16.12	0.855
3.764	2.988	0.794	7.53	6.37	0.846	18.82	16.68	0.886
3.764	2.746	0.730	7.53	5.94	0.789	18.82	17.01	0.904
3.764	2.748	0.730	7.53	6.14	0.816	18.82	17.30	0.919
3.764	2.723	0.723	7.53	6.12	0.814	18.82	16.75	0.890
3.764	2.848	0.757	7.53	6.02	0.800	18.82	17.54	0.932
Mean**		0.751			0.811			0.898
S***		0.027			0.020			0.027

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
98.3	91.8	195.8	183.5	392	405
98.3	88.6	195.8	191.3	392	411
98.3	91.3	195.8	185.0	392	373
98.3	94.1	195.8	189.4	392	396
98.3	86.0	195.8	177.8	392	405
98.3	87.4	195.8	171.5	392	377
Mean**	89.9		183.1		395
S***	3.04		7.39		15.9
Error (%)****	-8.5		-6.5		+0.8

*D.E. = mg found/mg taken **Mean - Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

Cyclohexanone

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 0.804 - 0.280\ X_{1i} + 0.00579\ X_{2i}$$

t-values -1.717 2.586

Sampling and Analysis:

$$Y = 0.840 + 3.37\ X_{1i} + 0.00041\ X_{2i}$$

t-values 0.462 2.146

Coefficients of Variation:

$CV_1^2 = 0.00063$ Analysis

$CV_2^2 = 0.00131$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0617$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: 2-Pentanone, No. S20

OSHA Standard: 705 mg/cu m

Chemical used for validation: 2-Pentanone, MC/B, Lot 8

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 2-pentanone in air is described in NIOSH Method S20, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S20. Samples of 2-pentanone in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 53.4 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of 2-pentanone in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 53.4 minutes). The "true" value for the concentration of 2-pentanone generated was calculated from vapor pressure of 30 mm Hg at 20°C supplied by J. T. Baker Chemical Co.

Modifications of P&CAM 127

This method worked satisfactorily for 2-pentanone.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2.) Breakthrough occurred in 100 minutes when a concentration of 1450 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

2-Pentanone

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
3.49	3.00	0.860	6.99	6.48	0.927	13.97	12.85	0.920
3.49	3.00	0.859	6.99	6.41	0.917	13.97	13.05	0.934
3.49	2.99	0.855	6.99	6.58	0.942	13.97	13.00	0.930
3.49	2.91	0.833	6.99	6.35	0.909	13.97	13.14	0.940
3.49	2.97	0.849	6.99	6.50	0.931	13.97	13.13	0.940
3.49	2.94	0.840	6.99	6.50	0.930	13.97	12.98	0.929
Mean**		0.849			0.926			0.932
S***		0.011			0.012			0.008

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
395	376	786	811	1570	1603
395	392	786	789	1570	1742
395	399	786	761	1570	1601
395	383	786	773	1570	1680
395	399	786	766	1570	1482
395	396	786	754	1570	1617
Mean**	391		776		1621
S***	9.4		21.0		87.0
Error (%)****	-1.0		-1.3		+3.2

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

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2 - Pentanone

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 0.597 + 0.1743\ X_{1i} + 0.2318\ X_{2i}$$

t-values: 0.01712 0.01799

Sampling and Analysis:

$$Y = 0.890 + 26.84\ X_{1i} + 0.00008\ X_{2i}$$

t-values 0.867 1.600

Coefficients of Variation:

$CV_1^2 = 0.00013$ Analysis

$CV_2^2 = 0.00146$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0630$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: p-tert-Butyltoluene, No. S22

OSHA Standard 60 mg/cu m

Chemical used for validation: p-tert-butyltoluene, MC/B, Lot 4

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of p-tert-butyltoluene in air is described in NIOSH Method S22, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S22. Samples of p-tert-butyltoluene in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 52.6 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of p-tert-butyltoluene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 52.6 minutes). The "true" value for the concentration of p-tert-butyltoluene generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for p-tert-butyltoluene. The only modification made was in the preparation of the charcoal tubes for desorption efficiency tests. A hexane solution of p-tert-butyltoluene containing 77.5 mg/ml was used to apply the analyte to the charcoal. This was done so it would not be necessary to use injections less than 2 µl.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-Butanone. (Reference 2) Breakthrough occurred in 231 minutes when a concentration of 112 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. A hexane solution of p-tert-butyltoluene containing 77.5 mg/ml was used to inject the p-tert-butyltoluene onto the charcoal. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

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Laboratory Results

p-Tert-Butyltoluene

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
0.2715	0.2877	1.060	0.5430	0.5770	1.063	1.086	1.133	1.043
0.2715	0.2862	1.054	0.5430	0.5803	1.069	1.086	1.128	1.039
0.2715	0.2796	1.030	0.5430	0.6131	1.129	1.086	1.142	1.051
0.2715	0.2874	1.059	0.5430	0.6076	1.119	1.086	1.098	1.011
0.2715	0.2911	1.072	0.5430	0.5834	1.074	1.086	1.148	1.057
0.2715	0.2945	1.085	0.5430	0.6084	1.120	1.086	1.114	1.026
Mean**		1.060			1.096			1.038
S***		0.018			0.030			0.017

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
29.0	27.31	58.0	51.03	119	108.9
29.0	26.16	58.0	54.07	119	108.4
29.0	23.29	58.0	55.22	119	109.1
29.0	26.70	58.0	52.77	119	109.1
29.0	25.67	58.0	51.76	119	101.4
29.0	24.94	58.0	47.01	119	112.3
Mean**	25.68		51.98		108.2
S***	1.43		2.87		3.61
Error (%)****	-11.4		-10.4		-9.08

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

p-Tert-Butyltoluene

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 1.282 - 0.0466\ X_{1i} - 0.1850\ X_{2i}$$

t-values: -3.71 -4.33

Sampling and Analysis:

$$Y = 0.893 - 0.355\ X_{1i} + 0.00016\ X_{2i}$$

t-values -0.1399 0.2200

Coefficients of Variation:

$CV_1^2 = 0.00052$ Analysis

$CV_2^2 = 0.00193$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0666$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: Cumene, No. S23

OSHA Standard: 245 mg/cu m

Chemical used for validation: Cumene from Eastman Chemical Co., Lot A2C

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of cumene in air is described in NIOSH Method S23, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S23. Samples of cumene in dry air were generated by the procedure described below, and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 52.6 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of cumene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 52.6 minutes). The "true" value for the concentration of cumene generated was calculated as described below, using vapor pressure data. (Ref. 1)

Modifications of P&CAM 127

This method worked satisfactorily for cumene. The only modification made was in the preparation of the charcoal tubes for desorption efficiency tests. A hexane solution of cumene containing 247 mg/ml was used to apply the analyte to the charcoal. This was done so it would not be necessary to inject less than 2 µl at the 0.5X level.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2) Less than 5% of the generated concentration of 480 mg/cu m was present in the effluent after four hours sampling at a rate of 0.19 liter per minute, indicating a capacity of at least 22 mg of cumene for this charcoal.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. A hexane solution of cumene containing 247 mg/ml was used to inject the cumene onto the charcoal. Results are given in the **laboratory** data section of this report.

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Generation of Samples

The system for generating and collecting samples of vapor from volatile liquids consists basically of a sample generator, a mixing and dilution section, and three sampling chambers. Samples are generated at a concentration 2 times the OSHA standard, serial dilutions are made to 1 times and 0.5 times the standard, and samples are collected simultaneously at the three concentrations.

A 500-ml three-neck round bottom flask containing the liquid analyte serves as a sample generator. The flask is fitted with a condenser water-cooled to a known temperature. One neck holds a thermometer immersed in the liquid, which is maintained at a constant temperature below its boiling point. An accurately measured flow of nitrogen gas enters the other inlet of the flask and sweeps the vapors out of the flask, through the fixed temperature condenser, into the mixing area where they are diluted with dry air to the concentration of 2 times the OSHA standard. This is referred to as the primary dilution.

Two sets of matched orifices are used to pull the vapors into the sampling chambers and to make the necessary secondary dilutions so that the concentrations in the three chambers are at 2X, 1X and 0.5X the OSHA standard.

After primary dilution, the vapor at 2X the standard concentration enters a stainless steel transfer line, the other end of which is connected to a pump through a critical orifice. The three sampling chambers branch off this line. The generated vapor is split at the first sampling chamber by a pump connected through a critical orifice to the bottom of the first chamber. This chamber now contains an atmosphere at 2X the standard as generated. Diluting air enters the transfer line immediately following the branch-off to the first chamber, mixes with the vapor sample, and the vapor at the new concentration of 1X the standard is again split by pumping into the second chamber. Another dilution is made in the transfer line following the second chamber, to obtain the concentration needed for the 0.5X level. A pump connected to the bottom of the third sampling chamber pulls sample at this concentration into this chamber

The two sets of orifices used to obtain these dilutions have been chosen so that the desired directions of flow are maintained in the system, and so the appropriate dilutions are made between the first and second, and second and third chambers. The orifices connected to the outlet of the transfer line and to the three sampling chambers operate at 13 liters per minute. The pressure of the secondary dilution air entering the line between the chambers is set so each orifice admits air at a flow of 13 liters per minute.

The three sampling chambers are identical. Each consists of a stainless steel cone, the top of which is connected to the transfer

line, and the bottom of which is fitted to a cylindrical section. The base of the cylindrical section contains the fittings necessary to hold six samples in a vertical position, plus a centered outlet to the pump mentioned above. The six sample ports are connected through six matching critical orifices to a sampling pump. A separate metal bellows vacuum pump is used for sampling each chamber.

Generation of vapors at the desired concentration is accomplished by adjusting the flows of nitrogen gas through the generating flask and of the primary dilution air. Adjustments for further dilutions to the 1X and 0.5X levels are not necessary since this secondary dilution is controlled automatically by the system of orifices described above.

To determine the ratio of flow rates for the 2X concentration, Equation (2) of the attached write-up entitled "Calculations of Vapor Generation of Volatile Liquids" is used. This calculation can be done accurately when the vapor pressure of the analyte is known at the temperature of the condenser head. If this is the case, the concentration in the 2X chamber can be calculated and this figure used for the "true" generated concentration. Multiplication of this by 0.5 gives the concentration of the 1X chamber; multiplication of the concentration of the 1X chamber by 0.5 gives the concentration of the 0.5X chamber.

In instances where the vapor pressure of the analyte is not known, an estimation of the desired flow rates of nitrogen and primary diluting air can be made by extrapolating from vapor pressure data of similar compounds. In this case, the concentration of the atmosphere in the chambers must be measured, and adjustment of the flow rates made until the required concentration is reached.

Each of the sampling chambers is fitted with an outlet which is connected to a gas chromatograph through a stainless steel line. A 4-way valve in the line allows switching the gas chromatograph connection to any of the chambers. A small pump operating at approximately 0.2 liter per minute pulls sample from the chamber into a gas sampling inlet of the gas chromatograph. After flushing of the line an aliquot is taken for analysis. The sampled atmosphere (except for the small aliquot used for analysis) is returned to the effluent from the sampling chamber. The concentration is determined by comparison with a "bag" standard, which is a known concentration of the vapor in dry air, prepared by injecting a known amount of the analyte into a measured amount of air. (This is done by allowing a stream of air at 1 liter per minute to flow into a plastic bag past an injection port while slowly adding the analyte through the injection port from a syringe of suitable size.) The "bag" standard is sampled into the gas chromatograph through the same gas inlet tube as is used for the sampling chamber measurements.

When the desired concentration has been reached, sampling is initiated by activating the three sampling pumps connected to the 18 sample tubes. Each of the samples is collected for the same length of time.

The volumes for each of the individual samples are calculated by multiplying the sampling time by the flow rate of the orifice used, thus correcting for the small variations in the critical orifices.

The "true" cumene concentrations were calculated from vapor pressure data by means of Equation (2) of the attached writeup. The condenser head temperature was 20°C, mixing chamber temperature was 23°C, the atmospheric pressure was 763.3 mm Hg, the nitrogen flow was 0.714 liter per minute and diluting air flow was 33.0 liter per minute.

A "bag" standard of cumene in dry air was also prepared using 6 µl of cumene in 10 liters of air, which is a concentration of 518 mg/cu m. Measurement of the concentration of cumene in the 2X chamber and comparison with the bag standard indicated a concentration of 471 mg/cu m in the chamber.

References

1. Vapor pressure data obtained from Perry's Chemical Engineers' Handbook, 4th ed., McGraw-Hill.

2. Backup Data Report for 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

3. Attachment, "Calculations of Vapor Generation of Volatile Liquids."

Calculations for Vapor Generation of Volatile Liquids

The vapor generator consists of a heated roundbottom flask fitted with a simple open tube bubbler for nitrogen and a condenser that is held at a constant temperature that is approximately 5°C below room temperature. The temperature of the liquid in the flask should be at least 20°C above the condenser temperature and a few degrees below its normal boiling point. The condenser temperature (T,°K) should be recorded to the nearest 0.1°.

The output of the vapor generator is mixed with air to get the desired vapor concentration in air in the sample generator which consists of the vapor generator, mixing chamber, and sampling ports.

The following equation gives the relationship between the vapor concentration in the sample generator and the measured parameters:

$$C = \frac{F_1 P_0 P_1 T_5 P_2 MWT\ 40.87}{F_1 P_0^2 T_5^2\ 2.55 + F_5 P_2^2 T_4 (P_0 - P_1)} \qquad (1)$$

C = mg/liter

P_0 = atmospheric pressure (mm)

P_1 = vapor pressure (mm) at T_1

P_2 = absolute pressure in mixing chamber (mm)

T_1 = condenser temperature (°K)

T_4 = room temperature (°K)

T_5 = temperature in mixing chamber (°K)

MWT = molecular weight (g/mole)

F_1 = flow rate of N_2 into generator (liter/minute)

F_5 = flow rate of air into generator (liter/minute)

If $P_0 = P_2$ and $T_5 = T_4$, equation (1) becomes

$$C = \frac{F_1 P_1 MWT \times 40.87}{F_1 T_5 \times 2.55 + F_5 (P_0 - P_1)} \qquad (2)$$

Rearrangement of equation (2) leads to equation (3) for the ratio of air to nitrogen flow rates.

$$\frac{F_5}{F_1} = \frac{P_1 MWT \times 40.87}{C(P_0 - P_1)} - \frac{T_5 \times 2.55}{(P_0 - P_1)} \qquad (3)$$

The last term in equation (3) is approximately 1.1 so

$$\frac{F_5}{F_1} \cong \frac{P_1 MWT \times 40.87}{C(P_0 - P_1)} - 1.1 \qquad (4)$$

Equation (4) is useful in setting up sample generation experiments. Equation (1) should be used to calculate exact values of expected vapor concentrations in the sample generator.

Laboratory Results

Cumene

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
0.865	0.903	1.044	1.730	1.714	0.991	3.46	3.57	1.031
0.865	0.914	1.056	1.730	1.769	1.023	3.46	3.58	1.036
0.865	0.910	1.052	1.730	1.745	1.009	3.46	3.58	1.035
0.865	0.923	1.067	1.730	1.727	0.999	3.46	3.55	1.025
0.865	0.931	1.076	1.730	1.759	1.017	3.46	3.54	1.025
0.865	0.906	1.047	1.730	1.755	1.014	3.46	3.58	1.036
Mean**		1.057			1.009			1.031
S***		0.012			0.012			0.005

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
120	127	240	261	479	489
120	125	240	256	479	520
120	130	240	250	479	496
120	131	240	250	479	509
120	129	240	244	479	459
120	129	240	246	479	503
Mean**	129		251		496
S***	2.17		6.34		21.0
Error (%)****	+7.5		+4.6		+3.5

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

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Cumene

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 2.534 - 0.794\ X_{1i} - 0.741\ X_{2i}$$

t-values: -0.0824 -0.0821

Sampling and Analysis:

$$Y = 1.020 + 7.68\ X_{1i} + 0.00001\ X_{2i}$$

t-values: 0.782 0.0455

Coefficients of Variation:

$CV_1^2 = 0.00010$ Analysis

$CV_2^2 = 0.00098$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0590$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: Vinyl Toluene, No. S25

OSHA Standard: 480 mg/cu m

Chemical used for validation: Vinyl Toluene, Dow Chemical Co. (60% meta, 40% para) (Stabilized with hydroquinone)

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of vinyl toluene in air is described in NIOSH Method S25, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S25. Samples of vinyl toluene in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 50 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of vinyl toluene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 50 minutes). The "true" value for the concentration of vinyl toluene generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for vinyl toluene.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone.(Reference 2). Breakthrough occurred in 188 minutes when a concentration of 952 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

Vinyl Toluene

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
2.411	1.994	0.827	4.82	4.19	0.869	9.64	8.70	0.902
2.411	1.951	0.809	4.82	4.21	0.873	9.64	8.81	0.914
2.411	1.990	0.825	4.82	4.28	0.888	9.64	8.79	0.912
2.411	1.989	0.825	4.82	4.24	0.879	9.64	8.73	0.906
2.411	1.997	0.828	4.82	4.23	0.878	9.64	8.67	0.899
2.411	1.985	0.823	4.82	4.27	0.886	9.64	8.71	0.904
Mean**		0.823			0.879			0.906
S***		0.007			0.007			0.006

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
256	239	506	478	970	928
256	243	506	472	970	974
256	239	506	452	970	935
256	222	506	468	970	954
256	230	506	458	970	946
256	231	506	422	970	915
Mean**	234		458		942
S***	8		20		21
Error(%)****	-8.6		-9.5		-2.9

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

Vinyl Toluene

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 0.747 + 0.1074\ X_{1i} + 0.1487\ X_{2i}$$

t-values: 0.0623 0.0640

Sampling and Analysis:

$$Y = 0.755 + 26.47\ X_{1i} + 0.00019\ X_{2i}$$

t-values 1.614 2.936

Coefficients of Variation:

$CV_1^2 = 0.00006$ Analysis

$CV_2^2 = 0.00089$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0582$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance:	Alpha-Methyl Styrene, No. S26
OSHA Standard:	480 mg/cu m (Ceiling)
Chemical used for validation	Alpha-Methyl Styrene, MC/B (Stabilized with hydroquinone)

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of alpha-methyl styrene in air is described in NIOSH Method S26, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S26. Samples of alpha-methyl styrene in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 15 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of alpha-methyl styrene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 15 minutes). The "true" value for the concentration of alpha-methyl styrene generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for alpha-methyl styrene.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2) Less than 5% of the generated concentration of 940 mg/cu m was present in the effluent after four hours sampling at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

α-Methyl Styrene

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
0.687	0.629	0.914	1.375	1.251	0.910	3.57	3.29	0.922
0.687	0.631	0.918	1.375	1.237	0.900	3.57	3.29	0.922
0.687	0.617	0.898	1.375	1.236	0.899	3.57	3.33	0.933
0.687	0.632	0.920	1.375	1.246	0.906	3.57	3.32	0.930
0.687	0.643	0.936	1.375	1.261	0.917	3.57	3.34	0.936
0.687	0.617	0.898	1.375	1.247	0.907	3.57	3.36	0.941
Mean**		0.914			0.906			0.931
S***		0.014			0.0066			0.0076

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
236	234	471	424	943	823
236	230	471	443	943	892
236	233	471	421	943	846
236	231	471	411	943	871
236	224	471	436	943	863
236	220	471	386	943	856
Mean**	229		420		858
S***	5.5		20		23
Error (%)****	-3.0		-10.8		-8.9

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

α - Methyl Styrene

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 7.98 - 3.21\ X_{1i} - 3.79\ X_{2i}$$

t-values: -0.0864 -0.0864

Sampling and Analysis:

$$Y = 0.742 + 46.5\ X_{1i} + 0.00013\ X_{2i}$$

t-values 4.93 2.98

Coefficients of Variation:

$CV_1^2 = 0.00012$ Analysis

$CV_2^2 = 0.00039$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0538$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance:	Terphenyls, No. S27
OSHA Standard:	1 ppm (10 mg/cu m) - Ceiling
Chemical used for validation:	o-Terphenyl, Lot No. 711-AB Eastman Chemical Company

Procedure

The general procedure used is described in NIOSH Method No. S27, which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for gas chromatographic analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 15-minute sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot (5, 10, and 20 microliters) of a 13.55 mg/ml solution of o-terphenyl in hexane was added to 37-mm type AA Millipore filters. Ortho-terphenyl was extracted from the filter with carbon disulfide and analyzed in a Perkin Elmer Model 3920 Gas Chromatograph with a flame ionization detector. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S27.

Test atmospheres of o-terphenyl at concentrations at 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on the Millipore filters in open-faced polystyrene filter cassettes. The results of analysis of these samples are given in the Sampling and Analysis table. The estimated average size of the particles was 1 micron diameter. The collection efficiency at 2X the OSHA standard was measured for particles which might have passed through the first filter. The collection efficiency for particles was considered to be 1.00 ± 0.01.

Modification

The method used for Sampling and Analysis was a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for gas chromatographic analysis of organic samples.

Generation

Samples of o-terphenyl in air were generated by the procedure described in the attachment to this report.

A 0.25% solution of o-terphenyl in toluene (2.5 g of ortho-terphenyl made up to a 1-liter volume with toluene) was used in the aspiration system. Samples of o-terphenyl were generated and collected separately at each of three levels, 0.5X, 1X, and 2X the OSHA standard.

The output of the aspirator was diluted with air at a rate of 31 liters/minute to get the 2X level. A lower aspirator output was diluted by 41 liters/minute and 82 liters/minute to get the 1X and 0.5X levels, respectively.

Samples were collected and analyzed to monitor the concentration in the sampling chamber at each of the three levels. When the desired concentration was reached, six samples at each level were collected. Samples were collected for 15 minutes at a rate of approximately 1 liter/minute in open faced filter cassettes. Since the collection efficiency was found to be 1.00 $\pm$ 0.01, the concentration in the generator and the "found" concentrations were considered to be equal.

Particle size was determined by generation of ammonium fluorescein particles from a 0.25% solution of ammonium fluorescein in water (2.5 g of ammonium fluorescein made up to a 1-liter volume with water) and collection on 0.2-micron nucleopore filters. The filters were examined by optical microscopy under uv light. A mean particle size of 1 micron was found.

Collection Efficiency

The concentration of o-terphenyl particulates could not be measured directly with either the gas chromatograph or the total hydrocarbon analyzer because the concentration was too low. Collection efficiency was determined by measuring the amount of particulates collected on each of two filters mounted back-to-back. No o-terphenyl was found on the backup filter. Thus, the collection efficiency of the filter was found to be 1.00 $\pm$ 0.01.

The collection efficiency experiment was done at a generated concentration of 18.81 mg/cu m. The results are given in the following table:

COLLECTION EFFICIENCY OF O-TERPHENYL IN MILLIPORE FILTERS

mg o-terphenyl in first filter	mg o-terphenyl in backup filter	Total mg	Collection Efficiency of first filter (%)
0.2799	-0-	0.2799	100
0.2787	-0-	0.2787	100
0.2831	-0-	0.2831	100

Analytical method recoveries were done at 1% of the 2X OSHA standard level. The results are given in the following table. These results, however, were not used since the amount of analyte found on the backup filters was not detected.

ANALYTICAL METHOD RECOVERIES OF O-TERPHENYL AT 0.02X OSHA STANDARD LEVEL

mg taken	mg found	A.M.R.
0.002710	0.002475	0.913
0.002710	0.002480	0.915
0.002710	0.002580	0.952
	Mean	0.927

Discussion

The original method for collecting and analyzing samples of o-terphenyl is given in P&CAM 127 which is a charcoal tube method for collection of organic vapors in air. In order to collect o-terphenyl on charcoal, at the 2X level solely as a vapor, o-terphenyl must have a vapor pressure of 1.52×10^{-3} mm Hg at 22°C. The vapor pressure of o-terphenyl at 22°C is 2.64×10^{-4} mm Hg. Ortho-terphenyl could therefore exist as a particulate and vapor and could not be efficiently collected on charcoal.

Preliminary work on charcoal Lot 105 was done to test if o-terphenyl vapor could be collected. Two sets of glass fiber filters (Gelman, Type A) followed by 2 sets of charcoal tubes were used to collect o-terphenyl samples at a concentration of 16.96 mg/cu m. After collection, both filters and charcoal tubes were analyzed, and o-terphenyl was not found on either of the charcoal tubes.

Desorption efficiency tests were done for o-terphenyl on charcoal Lot 105. The D.E.'s are given in the following table:

DESORPTION EFFICIENCY OF O-TERPHENYL ON CHARCOAL LOT 105

0.5X			1.0X			2.0X		
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
0.0675	0.0538	0.797	0.135	0.114	0.844	0.270	0.211	0.781
0.0675	0.0530	0.785	0.135	0.120	0.889	0.270	0.239	0.885
0.0675	0.0524	0.776	0.135	0.115	0.852	0.270	0.235	0.870
0.0675	0.0337	0.499	0.135	0.115	0.852	0.270	0.221	0.819
0.0675	0.0459	0.680	0.135	0.114	0.844	0.270	0.234	0.867
0.0675	0.0500	0.741	0.135	0.122	0.904	0.270	0.223	0.826
	Mean	0.713			0.864			0.841
	Std dev	0.113			0.026			0.039
	CV_1	0.158			0.030			0.046

Since o-terphenyl exists as a particulate at room temperature, a filter collection method was developed as described in NIOSH Method No. S27.

Precision and Accuracy

The statistical procedures used are described in Reference No. 1.

$\overline{CV}_1 = 0.052$ $\overline{CV}_2 = 0.080$ $\overline{CV}_T = 0.097$

Data Sheet: Terphenyls, S27

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.0678	0.0658	0.971	0.1355	0.1426	1.052	0.2710	0.2707	0.999
0.0678	0.0635	0.937	0.1355	0.1434	1.058	0.2710	0.2657	0.980
0.0678	0.0635	0.937	0.1355	0.1301	0.960	0.2710	0.2391	0.882
0.0678	0.0655	0.966	0.1355	0.1234	0.911	0.2710	0.2730	1.007
0.0678	0.0653	0.963	0.1355	0.1300	0.959	0.2710	0.2733	1.008
0.0678	0.0631	0.931	0.1355	0.1218	0.899	0.2710	0.2797	1.032
n =		6			6			6
mean		0.951			0.973			0.985
std dev		0.018			0.068			0.053
CV_1		0.019			0.070			0.054

$\overline{CV}_1$ 0.052

$\overline{CV}_{A+\overline{DE}}$ 0.056

A curve of analytical method recovery versus mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Terphenyls, S27

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.0734	0.0772	14.85	5.20
	0.0578	0.0608	14.91	4.08
	0.0678	0.0713	14.99	4.76
	0.0610	0.0641	14.31	4.48
	0.0544	0.0572	14.06	4.07
	(Sample was lost.)			
			n = 5	
			mean	4.52
			std dev	0.48
			CV_2	0.106
1S	0.1226	0.1263	14.85	8.51
	0.1061	0.1097	14.99	7.32
	0.1143	0.1181	15.24	7.75
	0.1086	0.1123	14.31	7.85
	0.1142	0.1180	14.06	8.39
	(Sample was lost.)			
			n = 5	
			mean	7.96
			std dev	0.49
			CV_2	0.062
2S	0.306	0.310	14.85	20.88
	0.312	0.317	14.91	21.26
	0.260	0.264	14.99	17.61
	0.292	0.296	15.24	19.42
	0.296	0.300	14.31	20.96
	0.273	0.278	14.06	19.77
			n = 6	
			mean	19.98
			std dev	1.37
$\overline{CV}_2$ 0.080			CV_2	0.069

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Generation of Organic Particulates

Test atmospheres of organic particulates can be generated by an aspiration/spray-dry technique. The generation system (Figure 1) consists of a fluid aspirator, an impactor and cyclone which remove droplets greater than 6 microns, and a dilution chamber where solvent evaporates from the aerosol droplets. The entire system is made of Pyrex glass.

The aspiration unit (Figure 2) consists of a 0.5-mm capillary tube and a concentric outer tube. The tip of the 0.5-mm capillary tube is ground until the wall thickness at the exit of the tube is no more than 0.25 mm. The end of the outer tube is tapered so that the clearance between the tip of the capillary tube and the concentric outer tube is about 0.5 mm. The aspirator air at several psig passes through the outside tube at a high velocity. Liquid is drawn up the capillary tube and is aspirated at the tip where an aerosol is formed. The aerosol impacts on the roof of the primary separation chamber, where the largest droplets are removed. The remaining aerosol then passes into a cyclone which passes droplets less than about 6 microns. The large droplets which are impacted against the walls of the primary separation chamber and the cyclone, eventually reenter the liquid supply, thereby recycling of all unused solution.

The entire aspiration unit is preceded by a vapor saturation device (Figure 3). A round bottom flask is fitted with a coarse glass frit such that air may be bubbled through a solvent at rates up to 40 liters/minute. Air which is saturated with vapor of the particular solvent in use then passes through a cyclone to remove any droplets above 2 microns. Vapor exiting from the cyclone then enters the aspiration unit.

Recycling the impacted aerosol and presaturation of the aspirator air minimize the increase in the solution concentration due to vaporization of the solvent. Increased solution concentration would cause the aerosol particle size to increase as a function of time, which in turn would lead to an increase in the concentration of the aerosol particles. Tests have shown that generation periods of up to 8 hours with this generator are possible with no significant change in the aerosol concentration.

Aerosol droplets enter the dilution chamber through an 18-mm O.D. tube which is concentric with a 20-mm I.D. tube which delivers the dilution air. Dilution air enters the chamber at a high velocity where turbulent mixing of the dilution air and the aerosol takes place. The residence time in the dilution chamber is sufficient for solvent evaporation from the droplets to occur.

As shown in Figure 1, dry particles in the glass dilution chamber are pulled into the sampling cone (Figure 4) at a rate of approximately 14 liters/minute (controlled by a 0.052-in critical orifice under a 25-in vacuum). Thus, it is necessary to have a total air flow of at least 25 liters/minute in the dilution chamber when a sample is being taken.

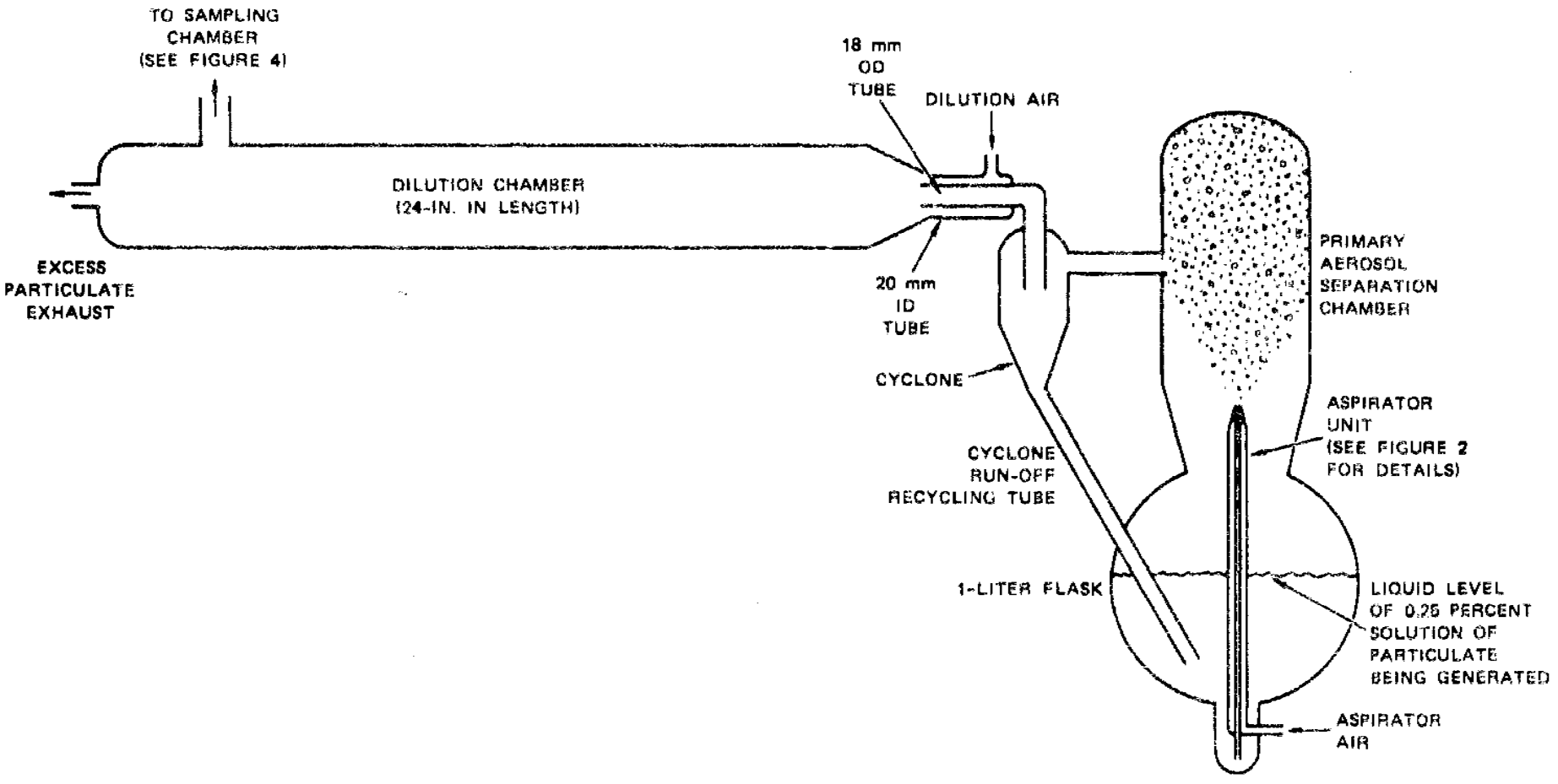
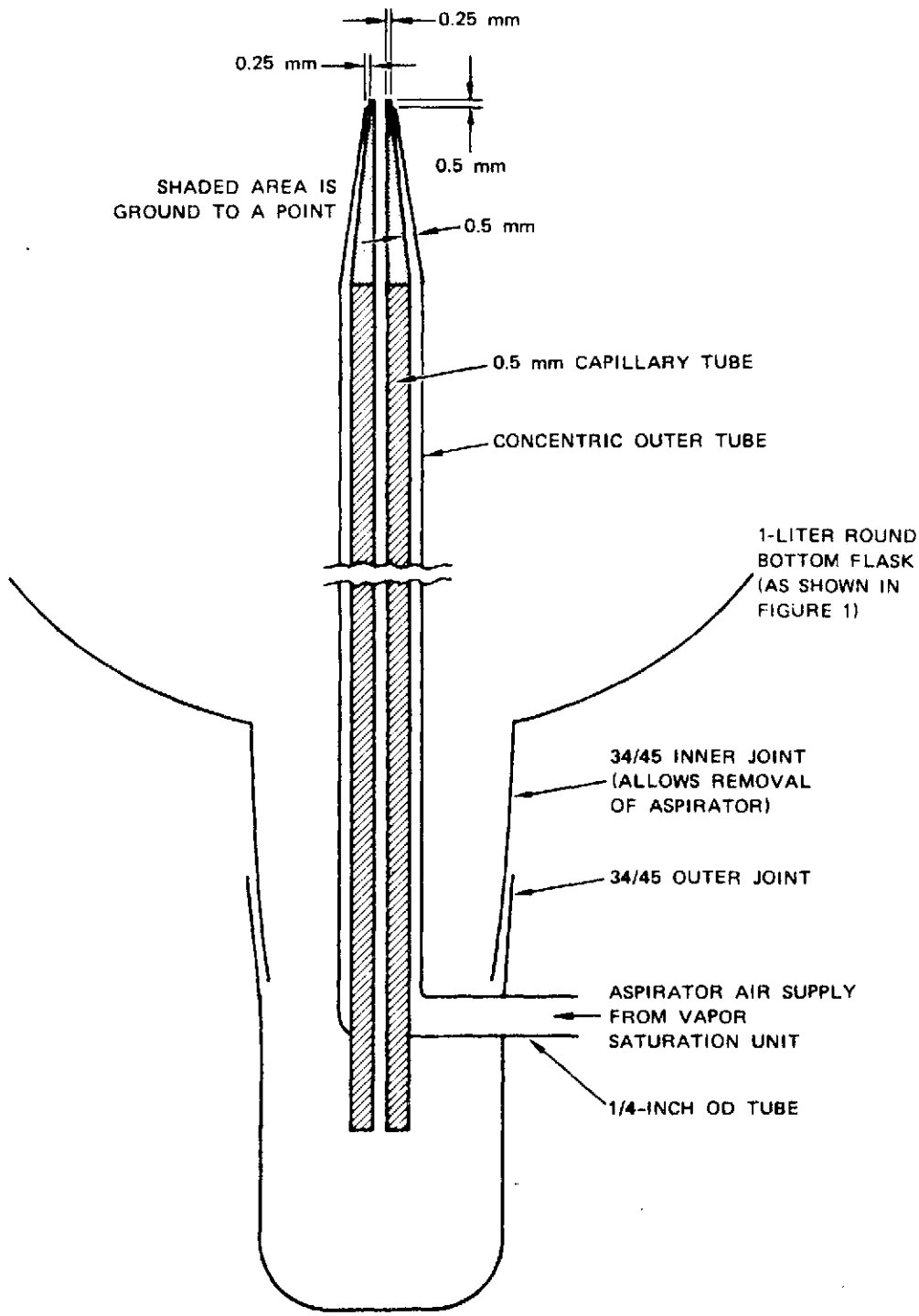


FIGURE 1 PARTICULATE GENERATION SYSTEM



NOTE: Total length of aspirator is 8 in.

SA-3516-8

FIGURE 2 DETAILS OF ASPIRATOR

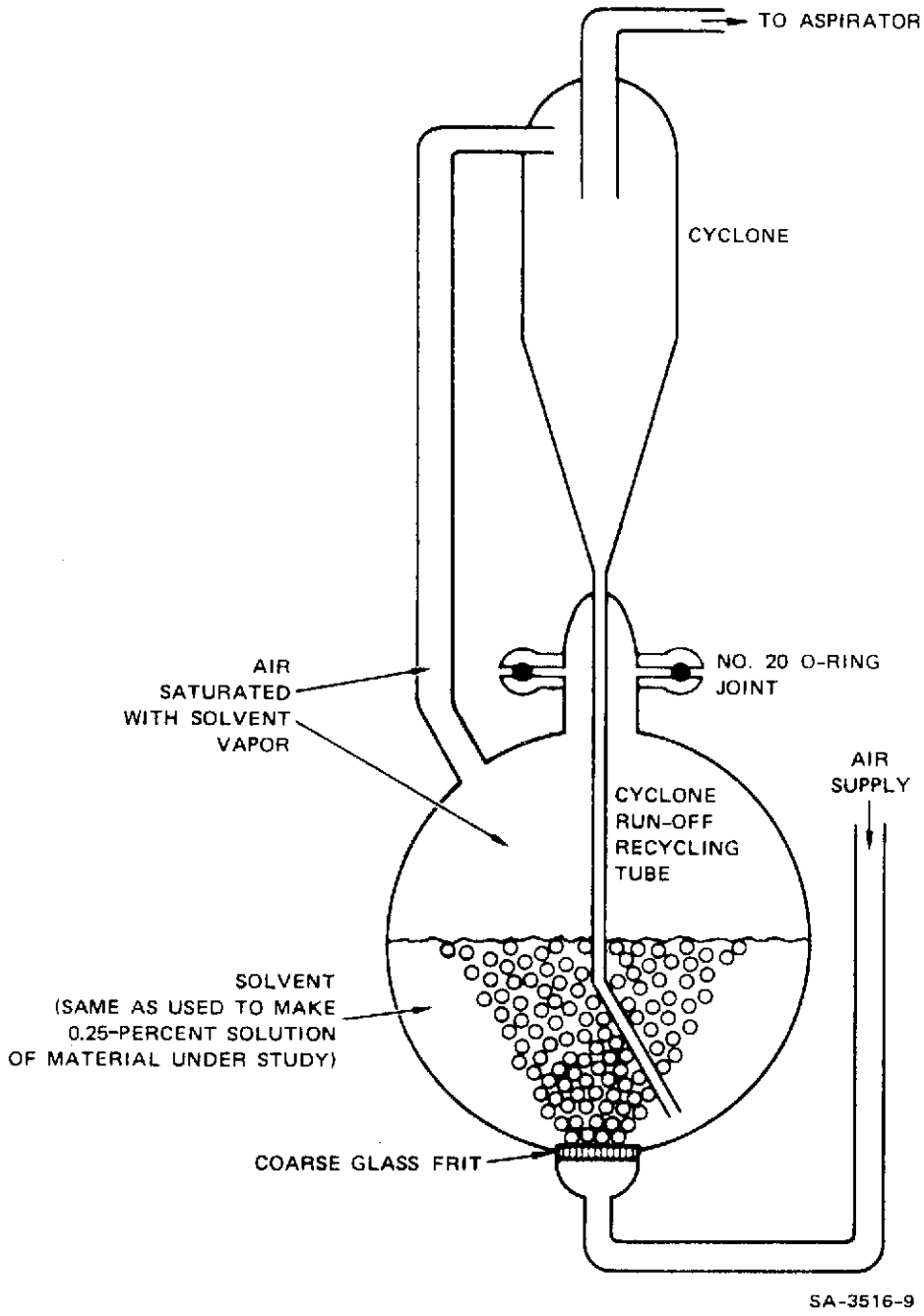


FIGURE 3 VAPOR SATURATION UNIT

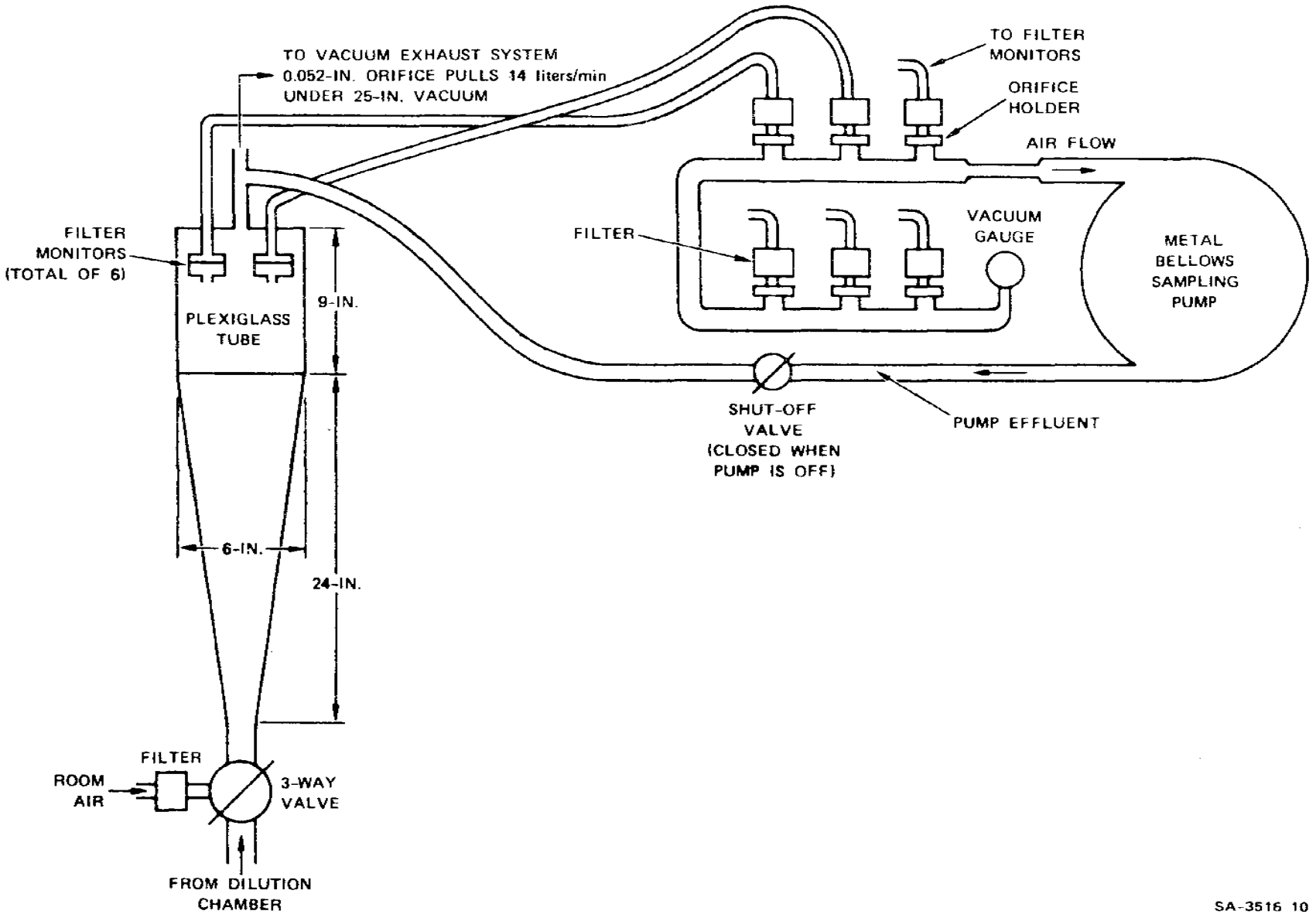


FIGURE 4 SAMPLING CHAMBER

The organic particulates move from the dilution chamber into the sampling chamber via a 3-way valve. The valve, when switched to a bypass mode, allows complete flushing of the sample chamber with room air after a sample run is completed. This further reduces possible exposure to toxic substances. The stainless steel sampling chamber is in the shape of an inverted cone approximately 2 ft high by 6 in diameter at the base. The base contains the fittings necessary to connect 6 filter holders in a vertical position. Six sampling ports were connected through individual critical orifices to a metal bellows pump. The effluent from the sampling pump is added back into the manifold that follows the sampling chamber but before the 0.052-in orifice. In this way, the total flow through the sampling cone is not disturbed while samples are being collected.

The entire system is kept under a slight vacuum (at least in a 1/2-in of water) during sampling to eliminate the possibility of toxic substance leaking into the laboratory. All of the solvent vapor, excess particulate, and sampling pump effluent is transported into the exhaust system of the main vapor generator unit.

Backup Data Report

Substance: Cyclohexane, No. S28

OSHA Standard: 1030 mg/cu m

Chemical used for validation: Cyclohexane, Baker A. R.

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of cyclohexane in air is described in NIOSH Method S28, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S28. Samples of cyclohexane in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 13.0 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of cyclohexane in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 13.0 minutes). The "true" value for the concentration of cyclohexane generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for cyclohexane.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2) Breakthrough occurred in 40 minutes when a concentration of 1650 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

Cyclohexane

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
1.32	1.43	1.08	2.65	2.76	1.04	5.30	5.51	1.04
1.32	1.39	1.05	2.65	2.90	1.09	5.30	5.56	1.05
1.32	1.36	1.03	2.65	2.83	1.07	5.30	5.54	1.04
1.32	1.43	1.08	2.65	2.89	1.09	5.30	5.47	1.03
1.32	1.33	1.00	2.65	2.80	1.06	5.30	5.49	1.04
1.32	1.44	1.09	2.65	2.72	1.03	5.30	5.56	1.05
Mean**		1.06			1.06			1.04
S***		0.035			0.025			0.008

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
509	492	998	1056	2009	2044
509	500	998	1100	2009	2328
509	491	998	1063	2009	2178
509	486	998	1045	2009	2221
509	495	998	1035	2009	2298
509	494	998	1014	2009	2169
Mean**	493		1052		2206
S***	4.6		29		102
Error (%)****	-3.1		+5.4		+9.8

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100 (Found - Taken)/Taken

Cyclohexane

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 4.89 - 1.954\ X_{1i} - 1.933\ X_{2i}$$

t-values: -0.00004 -0.00005

Sampling and Analysis:

$$Y = 1.231 - 124.5\ X1i - 0.00004\ X_{2i}$$

t-values: -2.736 -0.805

Coefficients of Variation:

$CV_1^2 = 0.00069$ Analysis

$CV_2^2 = 0.00187$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0661$

where

$$CV_T^2 = CV_2^2 + CV_P2$$

Backup Data Report

Substance: Ethyl Benzene, No. S29

OSHA Standard: 435 mg/cu m

Chemical used for validation: Ethyl Benzene, MC/B

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of ethyl benzene in air is described in NIOSH Method S29, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S29. Samples of ethyl benzene in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 50 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of ethyl benzene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 50 minutes). The "true" value for the concentration of ethyl benzene generated was calculated from vapor pressure of 7.01 mm Hg @ 20°C obtained from Perry's Chemical Engineers' Handbook.

Modifications of P&CAM 127

This method worked satisfactorily for ethyl benzene.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2). Breakthrough occurred in 186 minutes when a concentration of 917 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

Ethyl Benzene

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS					
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
2.168	2.293	1.058	4.34	4.69	1.082	8.67	8.96	1.033
2.168	2.302	1.062	4.34	4.70	1.085	8.67	9.13	1.053
2.168	2.277	1.050	4.34	4.61	1.063	8.67	9.14	1.055
2.168	2.259	1.042	4.34	4.66	1.074	8.67	9.12	1.052
2.168	2.285	1.054	4.34	4.68	1.080	8.67	9.10	1.049
2.168	2.294	1.058	4.34	4.64	1.069	8.67	9.34	1.076
Mean**		1.054			1.076			1.053
S***		0.0072			0.0084			0.014

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
221.9	194.6	442	423	884	778
221.9	145.2	442	419	884	855
221.9	191.6	442	410	884	818
221.9	178.1	442	404	884	839
221.9	207.3	442	405	884	816
221.9	191.3	442	374	884	831
Mean**	184.7		406		823
S***	21.5		17.3		26.2
Error (%)****	-16.8		-8.14		6.90

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

Ethyl Benzene

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 1.158 - 0.1802\ X_{1i} - 0.00970\ X_{2i}$$

t-values -4.03 -4.07

Sampling and Analysis:

$$Y = 1.066 - 47.4\ X_{1i} - 0.00009\ X_{2i}$$

t-values -1.665 -0.639

Coefficients of Variation:

$CV_1^2 = 0.00010$ Analysis

$CV_2^2 = 0.00393$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0411$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: Styrene, No. S30

OSHA Standard: 850 mg/cu m (Ceiling)
425 mg/cu m (T.W.A.)

Chemical used for validation: Styrene, 99%, Aldrich Chem. Co., Lot 021547 (Stabilized with hydroquinone)

General Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of styrene in air is described in NIOSH Method S30, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by the method described in S30. Samples of styrene in dry air were generated by the procedure described in the Backup Data Report for cumene, (Reference No. 1) and these samples were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Samples were collected for 25 minutes at a rate of approx. 0.2 liter per minute (individual critical orifices vary slightly in flow rate). The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of styrene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 25 minutes). The "true" value for the concentration of styrene generated was determined by comparison with a "bag" standard as described in Reference No. 1.

Modifications of P&CAM 127

This method worked satisfactorily for styrene.

Breakthrough Tests

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone. (Reference 2) Breakthrough occurred in 111 minutes when a concentration of 1710 mg/cu m was sampled at a rate of 0.19 liter per minute.

Desorption Efficiencies

The analytical method was validated by performing desorption efficiency tests as described in the method. Results are given in the laboratory data section of this report.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.
2. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

Laboratory Results

Styrene

Analytical - Desorption Efficiencies (D.E.)*

0.5 OS			1.0 OS			2.0 OS		
mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.	mg Taken	mg Found	D.E.
2.167	1.858	0.857	4.24	3.82	0.901	8.49	7.90	0.931
2.167	1.877	0.866	4.24	3.74	0.882	8.49	7.85	0.925
2.167	1.915	0.884	4.24	3.79	0.892	8.49	7.81	0.921
2.167	1.916	0.884	4.24	3.78	0.890	8.49	8.04	0.947
2.167	1.846	0.852	4.24	3.68	0.868	8.49	7.91	0.932
2.167	1.900	0.877	4.24	3.71	0.874	8.49	7.92	0.933
Mean**		0.870			0.885			0.932
S***		0.014			0.012			0.0089

Sampling and Analysis (values in mg/cu m)

Taken	Found	Taken	Found	Taken	Found
426	394	844	781	1710	1595
426	375	844	771	1710	1680
426	394	844	774	1710	1623
426	386	844	755	1710	1637
426	397	844	741	1710	1684
426	390	844	700	1710	1594
Mean**	389		754		1636
S***	8.0		3.0		4.0
Error (%)****	-8.7		-10.7		-4.3

*D.E. = mg found/mg taken **Mean = Sum (D.E.)/n or Sum (Found)/n

***S = Standard Deviation ****Error (%) = 100(Found - Taken)/Taken

Styrene

Statistical Analysis

Regression Equations:

Analysis:

$$Y = 0.824 + 0.0427\ X_{1i} + 0.01198\ X_{2i}$$

t-values: 0.793 4.11

Sampling and Analysis:

$$Y = 0.726 + 59.1\ X_{1i} + 0.00011$$

t-values: 2.55 3.60

Coefficients of Variation:

$CV_1^2 = 0.00014$ Analysis

$CV_2^2 = 0.00072$ Sampling and Analysis

$CV_P^2 = 0.0025$ Pump Error

$CV_T = 0.0567$

where

$$CV_T^2 = CV_2^2 + CV_P^2$$

Backup Data Report

Substance: sec.-Amyl Acetate, No. S31
(2-Pentyl Acetate)

OSHA Standard: 650 mg/cu m

Chemical used for
validation: 2-Pentanol Acetate, Chemical Samples Co.

Procedure

The general procedure used is described in NIOSH Method No. S31 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of sec.-amyl acetate represented in a 10 liter air sample. The charcoal used was LOT 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using tridecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 149 mg/min of sec.-amyl acetate via a syringe injector to a dry air stream flowing at a rate of .102 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 30.6 mg of sec.-amyl acetate when a test atmosphere containing 1462 mg/cu m of sec.-amyl acetate in air was sampled at 0.19 liters per minute for 110 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV_1} = 0.0116 \qquad \overline{CV_2} = 0.0502 \quad CV_T = 0.0710$$

The average recovery of the generated samples over all levels was

95.9 ± 9%

The uncertainty in this value was computed from

$$\sqrt{\overline{CV_2}^2 + (0.07)^2} \left(\frac{100}{\% \text{ Recovery}}\right) 100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: sec-Amyl Acetate S31

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.30	3.01	0.912	6.60	6.09	0.923	13.0	12.9	0.992
3.30	2.94	0.891	6.60	6.03	0.914	13.0	12.8	0.985
3.30	2.90	0.879	6.60	6.06	0.918	13.0	12.9	0.992
3.30	2.97	0.900	6.60	6.02	0.912	13.0	12.7	0.977
3.30	2.96	0.897	6.60	6.09	0.923	13.0	12.9	0.992
3.30	2.93	0.888	6.60	5.86	0.888	13.0	12.9	0.992
n =		6			6			6
mean		0.895			0.913			0.988
std dev		0.0113			0.0131			0.00622
CV_1		0.0126			0.0143			0.00629

$\overline{CV}_1$ 0.0116

$\overline{CV}_{A+\overline{DE}}$ 0.0125

Data Sheet: sec-Amyl Acetate S31

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.11	3.46	10.0	346	349	99.1
	3.02	3.36	10.0	336	349	96.3
	3.17	3.52	10.0	352	349	101
	3.02	3.36	10.0	336	349	96.3
	3.13	3.48	10.0	348	349	99.7
	2.70	3.00	10.0	300	349	86.0
			n = 6			
			mean	336		96.4
			std dev	18.9		
			CV_2	0.0564		
1S	6.38	7.01	10.0	701	719	97.5
	6.11	6.71	9.91	677	719	94.2
	6.06	6.66	9.83	678	719	94.3
	6.19	6.80	10.2	667	719	92.8
	6.27	6.89	10.0	689	719	95.8
	5.42	5.96	9.96	598	719	83.2
			n = 6			
			mean	668		93.0
			std dev	36.4		
			CV_2	0.0544		
2S	14.7	14.8	10.3	1440	1460	98.6
	14.4	14.5	10.0	1450	1460	99.3
	14.2	14.3	10.0	1430	1460	98.0
	13.8	13.9	10.0	1390	1460	95.2
	14.2	14.3	10.4	1380	1460	94.5
	15.1	15.3	10.0	1530	1460	105
			n = 6			
			mean	1437		98.4
			std dev	53.5		
			CV_2	0.0373	$\overline{CV_2}$	0.0502

Backup Data Report

Substance: tert.-Butyl Acetate, No. S32

OSHA Standard: 200 ppm (950 mg/cu m)

Chemical used for validation: tert.-Butyl Acetate, Eastman Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S32 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of tert.-butyl acetate represented in a 10 liter air sample. The charcoal used was LOT 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 183 mg/min of tert.-butyl acetate via a syringe injector to a dry air stream flowing at a rate of .1028 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 25.4 mg of tert.-butyl acetate when a test atmosphere containing 1780 mg/cu m of tert.-butyl acetate in air was sampled at 0.19 liters per minute for 75 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV_1} = 0.0389 \qquad \overline{CV_2} = 0.0743 \quad CV_T = 0.0909$$

The average recovery of the generated samples over all levels was

$$91.5 \pm 11.2\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV_2}^2 + (0.07)^2} \left(\frac{100}{\%\ \text{Recovery}}\right) \quad 100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-]4-45.

Data Sheet: tert-Butyl Acetate S32

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.74	4.79	1.011	9.48	8.82	0.930	19.0	17.7	0.932
4.47	4.79	1.011	9.48	9.28	0.979	19.0	18.0	0.947
4.74	4.37	0.922	9.48	8.88	0.937	19.0	17.5	0.921
4.74	4.35	0.918	9.48	8.66	0.914	19.0	18.3	0.963
4.74	4.15	0.876	9.48	9.17	0.967	19.0	17.9	0.942
4.74	4.48	0.945	9.48	8.60	0.907	19.0	17.4	0.916
n =		6			6			6
mean		0.947			0.939			0.937
std dev		0.0541			0.0287			0.0175
CV_1		0.0571			0.0306			0.0186

$\overline{CV_1}$ 0.0389

$\overline{CV_{A+\overline{DE}}}$ 0.0420

Data Sheet: tert-Butyl Acetate S32

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.91	3.13	10.1	310	424	73.1
	3.54	3.81	10.1	377	424	88.9
	3.73	4.01	10.1	397	424	93.6
	3.79	4.08	10.1	404	424	95.3
	3.23	3.47	10.1	344	424	81.1
	3.77	4.05	10.1	401	424	94.6
			n = 6			
			mean	372		87.8
			std dev	37.8		
			CV_2	0.1016		
1S	1.43*	1.59*	10.1	157*	875	17.9*
	7.94	8.45	10.0	845	875	96.6
	7.39	7.86	9.95	790	875	90.3
	6.89	7.33	10.1	726	875	83.0
	7.77	8.27	10.2	811	875	92.7
	7.86	8.36	10.1	828	875	94.6
			n = 5			
			mean	800		91.4
			std dev	46.1		
			CV_2	0.0576		
2S	17.4	18.5	10.4	1780	1780	100
	15.3	16.3	10.2	1600	1780	89.9
	15.3	16.3	10.2	1600	1780	89.9
	15.9	16.9	10.1	1670	1780	93.8
	17.4	18.5	10.5	1760	1780	98.9
	17.0	18.1	10.2	1770	1780	99.4
			n = 6			
			mean	1697		95.3
			std dev	84.5		
			CV_2	0.0498	$\overline{CV}_2$	0.0743

*These values excluded from statistical analysis

Backup Data Report

Substance: Dibutyl Phthalate, No. S33

OSHA Standard: 5 mg/cu m

Chemical used for validation: n-Butyl Phthalate (Dibutyl Phthalate), Fisher Reagent

Procedure

The general procedure used is described in NIOSH Method No. S33 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 30 liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot (usually 2, 4 and 8 microliters) of a solution of the analyte in carbon disulfide was added to 37 mm Type AA Millipore filters. The analyte was extracted from the filter with carbon disulfide and analyzed in a Varian 2700 Gas Chromatograph with an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. All data are based on an internal standard approach using heneicosane as internal standard. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S33 and in the Butyl Acetate S47 Backup Data Report.

Generation

A test atmosphere was generated using the Royco generator/impinger system described in the 2-ethylhexyl phthalate S40 Backup Data Report and calibrated using the GC assay procedure. This test atmosphere was generated at 25°C and 767 mm Hg at a level of 408 mg/cu m and diluted 41.7 to 1 to produce a 2S level of 9.78 mg/cu m. The dilution ratios as determined by the aerosol photometer were 0.186, 0.450 and 1.00 to produce test levels of 1.82, 4.40 and 9.78 mg/cu m. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 28 minutes (30 liters). The 2S aerosol concentration was monitored throughout the calibration and collection and was observed to remain constant. The aerosol particle size is estimated to be at least less than 5 micrometers and probably closer to 0.3 micrometers diameter. Collection efficiency for aerosols such as this on Type AA filters is greater than 99.9%.

Discussion

Experiments on glass fiber filters spiked at concentrations equivalent to a 30-liter sample at the standard level and extracted with carbon disulfide using the pipet technique also gave low recoveries with poor precision, 63% $\pm$ 8%. The recoveries improved markedly, 97% $\pm$ 4%, when cellulose membrane filters were used, and there were no apparent sample losses for spiked samples stored for as long as six days.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0364 \qquad \overline{CV}_2 = 0.0269 \qquad \overline{CV}_T = 0.0570$$

The average recovery of the generated samples over all levels was

$$93.5 \pm 8.0$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Dibutyl Phthalate S33

Analysis

Level			1S			2S		
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
0.075	0.071	94.7	0.150	0.143	95.3	0.300	0.291	97.0
0.075	0.072	96.0	0.150	0.147	98.0	0.300	0.290	96.7
0.075	0.072	96.0	0.150	0.144	96.0	0.300	0.283	94.3
0.075	0.073	97.3	0.150	0.144	96.0	0.300	0.300	100.0
0.075	0.075	100.0	0.150	0.139	92.7	0.300	0.284	94.7
0.075	0.081	108.0	0.150	0.153	102.0	0.300	0.290	96.7
n =		6			6			6
mean		98.7			96.7			96.6
std dev		4.91			3.12			2.03
CV_1		0.0498			0.0323			0.0210

$\overline{CV}_1$ 0.0364

$\overline{CV}_{A+\overline{DE}}$ 0.0393

Data Sheet: Dibutyl Phthalate S33
Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.051	30.4	1.68	1.82	
	0.052	30.0	1.73	1.82	
	0.051	30.3	1.68	1.82	
	0.057	30.9	1.84	1.82	
	0.051	30.3	1.68	1.82	
	0.054	29.9	1.81	1.82	
		n = 6			
		mean	1.74		95.6
		std dev	0.0717		
		CV_2	0.0412		
1S	0.122	29.8	4.09	4.40	
	0.119	30.1	3.95	4.40	
	0.122	30.1	4.05	4.40	
	0.121	30.3	3.99	4.40	
	0.121	30.1	4.02	4.40	
	0.121	30.3	3.99	4.40	
		n = 6			
		mean	4.02		91.4
		std dev	0.0497		
		CV_2	0.0124		
2S	0.287	30.4	9.44	9.78	
	0.276	30.6	9.02	9.78	
	0.274	30.1	9.10	9.78	
	0.275	30.6	8.99	9.78	
	0.275	30.1	9.14	9.78	
	0.272	30.0	9.07	9.78	
		n = 6			
		mean	9.13		93.4
		std dev	0.163		
		CV_2	0.0178		
		$\overline{CV_2}$	0.0269		

Backup Data Report

Substance: Ethyl Acrylate, No. S35

OSHA Standard: 100 mg/cu m

Chemical used for validation: Ethyl Acrylate, Eastman Practical Grade (stabilized with hydroquinone)

Procedure

The general procedure used is described in NIOSH Method No. S35 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of ethyl acrylate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 21 mg/min of ethyl acrylate via a syringe injector to a dry air stream flowing at a rate of 0.0999 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 46 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 9.6 mg of ethyl acrylate when a test atmosphere containing 210 mg/cu m of ethyl acrylate in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0290 \qquad \overline{CV}_2 = 0.0174 \qquad CV_T = 0.0542$$

The average recovery of the generated samples over all levels was

$$92.9 \pm 7.8\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^{\,2} + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Ethyl Acrylate S35

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.462	0.427	0.924	0.924	0.874	0.946	2.03	1.89	0.931
0.462	0.429	0.929	0.924	0.873	0.945	2.03	1.90	0.936
0.462	0.456	0.987	0.924	0.933	1.010	2.03	1.91	0.941
0.462	0.467	1.011	0.924	0.903	0.977	2.03	1.88	0.926
0.462	0.454	0.983	0.924	0.864	0.935	2.03	1.89	0.931
0.462	0.445	0.963	0.924	0.870	0.942	2.03	1.81	0.892
n =		6			6			6
Mean		0.966			0.959			0.926
std dev		0.0343			0.0288			0.0175
CV_1		0.0356			0.0301			0.0189

$\overline{CV}_1$ 0.0290

$\overline{CV}_{A+\overline{DE}}$ 0.0313

Data Sheet: Ethyl Acrylate S35

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.419	0.441	10.0	44.1	50.0	88.2
	0.444	0.467	10.0	46.7	50.0	93.4
	0.443	0.466	10.0	46.6	50.0	93.2
	0.440	0.463	10.0	46.3	50.0	92.6
	0.442	0.465	10.0	46.5	50.0	93.0
	0.440	0.463	10.0	46.3	50.0	92.6
			n = 6			
			mean	46.1		92.2
			std dev	0.99		
			CV_2	0.0214		
1S	0.905	0.953	10.0	95.3	103	92.5
	0.905	0.953	9.92	96.1	103	93.3
	0.912	0.960	9.83	97.7	103	94.9
	0.924	0.973	10.2	95.4	103	92.6
	0.910	0.958	10.0	95.8	103	93.0
	0.932	0.981	9.96	98.5	103	95.6
			n = 6			
			mean	96.5		93.7
			std dev	1.32		
			CV_2	0.0137		
2S	1.93	2.03	10.3	197	210	93.8
	1.87	1.97	10.0	197	210	93.8
	1.87	1.97	10.0	197	210	93.8
	1.84	1.94	10.0	194	210	92.4
	1.94	2.04	10.4	196	210	93.3
	1.80	1.89	10.0	189	210	90.0
			n = 6			
			mean	195		92.9
			std dev	3.16		
			CV_2	0.0162		$\overline{CV}_2$ 0.0174

Backup Data Report

Substance: Ethyl Formate, No. S36

OSHA Standard: 300 mg/cu m

Chemical used for validation: Ethyl Formate, Eastman Practical Grade

Procedure

The general procedure used is described in NIOSH Method No. S36 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of ethyl formate represented in a 10 liter air sample. The charcoal used was LOT 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 4 times the OSHA standard level were generated by delivering 133 mg/min of ethyl formate via a syringe injector to a dry air stream flowing at a rate of 0.1017 cu m/min. The three sample lines were then maintained at dilution ratios of 0.1311, 0.2557 and 0.5097 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 9.5 mg of ethyl formate when a test atmosphere containing 666 mg/cu m of ethyl formate in air was sampled at 0.19 liters per minute for 75 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV_1} = 0.0189 \qquad \overline{CV_2} = 0.0596 \quad CV_T = 0.0782$$

The average recovery of the generated samples over all levels was

$$107.3 \pm 8.6\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV_2}^2 + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Ethyl Formate S36

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.48	1.12	0.757	2.96	2.41	0.814	5.91	5.08	0.860
1.48	1.14	0.770	2.96	2.46	0.831	5.91	5.13	0.868
1.48	1.15	0.777	2.96	2.50	0.845	5.91	5.17	0.875
1.48	1.17	0.791	2.96	2.41	0.814	5.91	5.11	0.865
1.48	1.12	0.757	2.96	2.37	0.801	5.91	5.06	0.856
1.48	1.19	0.804	2.96	2.38	0.804	5.91	5.09	0.861

n =	6	6	6
mean	0.776	0.818	0.864
std dev	0.0188	0.0168	0.00674
CV_1	0.0242	0.0206	0.00780

$\overline{CV}_1$ 0.0189

$\overline{CV}_{A+\overline{DE}}$ 0.0204

Data Sheet: Ethyl Formate S36

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.73	2.16	9.97	217	171	127
	1.65	2.06	9.97	207	171	121
	1.60	2.00	9.97	201	171	118
	1.58	1.98	9.97	199	171	116
	1.55	1.94	9.97	195	171	114
	1.63	2.04	9.97	205	171	120
			n = 6			
			mean	204		119
			std dev	7.67		
			CV_2	0.0376		
1S	2.88	3.47	9.97	348	334	104
	3.13	3.77	9.88	382	334	114
	2.94	3.54	9.80	361	334	108
	3.02	3.64	10.2	357	334	107
	2.83	3.41	10.0	341	334	102
	2.37	2.86	9.93	288	334	86.2
			n = 6			
			mean	346		104
			std dev	31.7		
			CV_2	0.0917		
2S	5.87	6.75	10.3	655	666	98.3
	5.42	6.23	10.0	623	666	93.5
	5.85	6.72	10.0	672	666	101
	5.86	6.74	9.97	676	666	102
	6.09	7.00	10.4	673	666	101
	5.73	6.59	10.0	659	666	98.9
			n = 6			
			mean	660		99.1
			std dev	19.8		
			CV_2	0.0300	$\overline{CV}_2$	0.0596

Backup Data Report

Substance: Methyl Isoamyl Acetate*, No. S37

OSHA Standard: 300 mg/ cu m

Chemical used for validation: 4-Methyl-2-Pentanol Acetate, Chemical Samples Co. 97%

Procedure

The general procedure used is described in NIOSH Method No. S37 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methyl isoamyl acetate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using dodecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 61.8 mg/min of methyl isoamyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1029 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 27.4 mg of methyl isoamyl acetate when a test atmosphere containing 601 mg/cu m of methyl isoamyl acetate in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

*Listed incorrectly as sec-Hexyl Acetate in 29 CFR 1910.93

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0206 \qquad \overline{CV}_2 = 0.0276 \qquad CV_T = 0.0577$$

The average recovery of the generated samples over all levels was

$$97.8 \pm 7.7\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^2 + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methyl Isoamyl Acetate S37

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.49	1.35	0.906	2.98	2.83	0.950	6.04	5.65	0.935
1.49	1.31	0.879	2.98	2.85	0.956	6.04	5.65	0.935
1.49	1.29	0.866	2.98	2.85	0.956	6.04	5.65	0.935
1.49	1.40	0.940	2.98	2.84	0.953	6.04	5.68	0.940
1.49	1.39	0.933	2.98	2.82	0.946	6.04	5.59	0.925
1.49	1.39	0.933	2.98	2.79	0.936	6.04	5.67	0.939
n =		6			6			6
mean		0.910			0.950			0.935
std dev		0.0312			0.00764			0.00531
CV_1		0.0343			0.00804			0.00568

$\overline{CV}_1$ 0.0206

$\overline{CV}_{A+\overline{DE}}$ 0.0222

Data Sheet: Methyl Isoamyl Acetate S37

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.26	1.38	10.1	137	143	95.8
	1.28	1.41	10.1	140	143	97.9
	1.33	1.46	10.1	145	143	101
	1.34	1.47	10.1	146	143	102
	1.29	1.42	10.1	141	143	98.6
	1.34	1.47	10.1	146	143	102
			n = 6			
			mean	143		99.6
			std dev	3.73		
			CV_2	0.0261		
1S	2.66	2.83	10.1	280	295	94.9
	2.70	2.87	10.0	287	295	97.3
	2.67	2.84	9.95	285	295	96.6
	2.66	2.83	10.3	275	295	93.2
	2.72	2.89	10.2	283	295	95.9
	2.67	2.84	10.1	281	295	95.3
			n = 6			
			mean	282		95.5
			std dev	4.22		
			CV_2	0.0150		
2S	5.77	6.14	10.4	590	600	98.3
	5.56	5.91	10.2	579	600	96.5
	6.02	6.40	10.2	627	600	105
	*	-	-	-	-	-
	5.64	6.00	10.5	571	600	95.2
	5.56	5.91	10.2	579	600	96.5
			n = 5			
			mean	589		98.3
			std dev	22.2		
			CV_2	0.0377	$\overline{CV}_2$	0.0276

*Sample lost

Backup Data Report

Substance: Methyl Acrylate, No. S38

OSHA Standard: 35 mg/cu m

Chemical used for validation: Methyl Acrylate, Eastman Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S38 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methyl acrylate represented in a 5 liter air sample. To minimize errors associated with volume measurements of less than 1 microliter, a solution of methyl acrylate in carbon disulfide was used. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 6.03 mg/min of methyl acrylate via a syringe injector to a dry air stream flowing at a rate of 0.1032 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 27 minutes (6 liters). This is the third set of 18 samples collected and these data have been used for the statistical analysis. The first set was for a 10 liter sample, and the data (CV_2 = 0.21, Recovery = 77%) suggest that the precision of the method is poor when as much as 0.5 mg (2S) of sample is collected on the charcoal. The second set, a reduction of the original sample size to 5 liters, was rejected because of poor precision apparently caused by five "outliers". Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 2.7 mg of methyl acrylate when a test atmosphere containing 59 mg/cu m of methyl acrylate in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0490 \qquad \overline{CV}_2 = 0.0376 \qquad \overline{CV}_T = 0.0656$$

The average recovery of the generated samples over all levels was

$$89.9 \pm 8.8\%$$

This low sample recovery could be due to polymerization losses during the sample generation and collection particularly for the higher sample concentrations.

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methyl Acrylate S38

Analysis

Level	0.5S			1S			2S		
	mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
	0.087	0.068	0.782	0.175	0.138	0.789	0.350	0.316	0.903
	0.087	0.067	0.770	0.175	0.147	0.840	0.350	0.293	0.837
	0.087	0.067	0.770	0.175	0.138	0.789	0.350	0.280	0.800
	0.087	0.071	0.816	0.175	0.132	0.754	0.350	0.302	0.863
	0.087	0.073	0.839	0.175	0.135	0.771	0.350	0.276	0.789
	0.087	0.077	0.885	0.175	0.134	0.766	0.350	0.299	0.854
	n =		6			6			6
	mean		0.810			0.785			0.841
	std dev		0.0458			0.0302			0.0422
	CV_1		0.0565			0.0385			0.0502

$\overline{CV_1}$ 0.0490

$\overline{CV}_A + \overline{DE}$ 0.0529

Data Sheet: Methyl Acrylate S38
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.065	0.080	6.02	13.3	13.9	95.7
	0.029*	0.036*	6.02	5.98*	13.9	
	0.063	0.078	6.02	13.0	13.9	93.5
	0.066	0.082	6.02	13.6	13.9	97.8
	0.065	0.080	6.02	13.3	13.9	95.7
	0.061	0.075	6.02	12.6	13.9	90.6
			n = 5			
			mean	13.2		95.0
			standard deviation	0.378		
			CV_2	0.0286		
1S	0.132	0.161	6.02	26.7	28.7	93.0
	0.124	0.151	5.97	25.3	28.7	88.2
	0.116	0.141	5.91	23.9	28.7	83.3
	0.115	0.140	6.13	22.8	28.7	79.3
	0.127	0.155	6.05	25.6	28.7	89.2
	0.125	0.152	5.99	25.4	28.7	88.5
			n = 6			
			mean	25.0		87.1
			standard deviation	1.38		
			CV_2	0.0552		
2S	0.260	0.313	6.21	50.4	58.4	86.3
	0.258	0.311	6.05	51.4	58.4	88.0
	0.257	0.310	6.05	51.2	58.4	87.7
	0.256	0.308	6.02	51.2	58.4	87.7
	0.262	0.316	6.26	50.5	58.4	86.5
	0.265	0.319	6.05	52.7	58.4	90.2
			n = 6			
			mean	51.2		87.7
			standard deviation	0.826		
			CV_2	0.0161		
			$\overline{CV_2}$	0.0376		

*These values excluded from statistical analysis

Backup Data Report

Substance: Methyl Cellosolve Acetate, No. S39

OSHA Standard: 120 mg/cu m

Chemical used for validation: 2-Methoxyethyl Acetate, Aldrich Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S39 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methyl cellosolve acetate represented in a 20 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

At the 10 liter sample size level, the desorption efficiency (DE) was 0.604, 0.723 and 0.809 at the 0.5, 1.0 and 2.0S levels respectively. Use of 10% methanol in carbon disulfide did not significantly improve these values (found 0.76 DE at the 1S level). Therefore a 20 liter sample size is recommended.

Modification

There were no modifications of P&CAM 127, except for an increase in sample size to 20 liters to accomodate desorption efficiency results.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 22 mg/min of methyl cellosolve acetate via a syringe injector to a dry air stream flowing at a rate of 0.1023 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 90 minutes (20 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 9.8 mg of methyl cellosolve acetate when a test atmosphere containing 214 mg/cu m of methyl cellosolve acetate in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0441 \qquad \overline{CV}_2 = 0.0416 \qquad CV_T = 0.0675$$

The average recovery of the generated samples over all levels was

$$99.8 \pm 8.2\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^{\,2} + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methyl Cellosolve Acetate S39

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.21	0.834	0.689	2.42	1.85	0.765	4.83	3.99	0.826
1.21	0.900	0.744	2.42	1.88	0.777	4.83	3.83	0.793
1.21	0.798	0.660	2.42	2.03	0.839	4.83	3.99	0.826
1.21	0.920	0.760	2.42	1.91	0.789	4.83	3.93	0.814
1.21	0.890	0.736	2.42	2.03	0.839	4.83	4.14	0.857
1.21	0.907	0.750	2.42	2.05	0.847	4.83	3.85	0.797
n =		6			6			6
mean		0.723			0.809			0.819
std dev		0.0396			0.0363			0.0234
CV_1		0.0548			0.0449			0.0285

$\overline{CV}_1$ 0.0441

$\overline{CV}_{A+\overline{DE}}$ 0.0476

Data Sheet: Methyl Cellosolve Acetate S39

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.665	0.950	20.0	47.5	51.0	93.1
	0.673	0.961	20.0	48.1	51.0	94.3
	0.589	0.841	20.0	42.1	51.0	82.5
	0.692	0.989	20.0	49.5	51.0	97.1
	0.717	1.02	20.0	51.0	51.0	100
	0.689	0.984	20.0	49.2	51.0	96.5
			n = 6			
			mean	47.9		93.9
			std dev	3.09		
			CV_2	0.0645		
1S	1.65	2.12	20.0	106	105	101
	1.63	2.09	19.9	105	105	100
	1.61	2.06	19.7	105	105	100
	1.66	2.13	20.4	104	105	99.0
	1.63	2.09	20.1	104	105	99.0
	1.60	2.05	20.0	103	105	98.1
			n = 6			
			mean	105		99.5
			std dev	1.049		
			CV_2	0.00999		
2S	3.76	4.59	20.7	222	214	104
	3.53	4.30	20.1	214	214	100
	3.78	4.61	20.1	229	214	107
	3.81	4.65	20.0	233	214	109
	3.91	4.77	20.8	229	214	107
	3.75	4.57	20.1	227	214	106
			n = 6			
			mean	226		106
			std dev	6.74		
			CV_2	0.0298	$\overline{CV}_2$	0.0416

Backup Data Report

Substance: Di-2-ethylhexyl Phthalate*, No. S40

OSHA Standard: 5 mg/cu m

Chemical used for validation: FLEXOL® Plasticizer DOP, Union Carbide (Di-2-ethylhexyl phthalate)

Procedure

The general procedure used is described in NIOSH Method No. S40 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 30 liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot (usually 2, 4 and 8 microliters) of a solution of the analyte in carbon disulfide was added to 37 mm Type AA Millipore filters. The analyte was extracted from the filter with carbon disulfide and analyzed in a Varian 2700 Gas Chromatograph with an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. All data are based on an internal standard approach using tricosane as internal standard. The final data presented are from the fourth set of 18 samples collected and the data from this set have been used for the statistical analysis. The other three sets of samples were collected from concentration levels considerably higher than the 0.5, 1 and 2 times the standard concentration. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S40 and in the Butyl Acetate S47 Backup Data Report.

Generation

A concentrated stream of di-2-ethylhexyl phthalate in air at room temperature and pressure was generated using a Royco Smoke and Aerosol Generator. The supporting literature states that this apparatus produces 0.3 micrometer median diameter aerosol. To further assure that no non-respirable size aerosol was added to the dilution system, the Royco output at a flow rate of 25 liters per minute was passed through a Greenburg-Smith impinger. Over the course of the run a small amount of liquid collected in the impinger.

* Listed incorrectly as di-sec-octyl phthalate in 29CFR 1910.93.

The mass concentration output of the aerosol stream emerging from the impinger was determined by collecting 3 - 4 samples on Type AA 37 mm filters for 15 - 30 minutes. The preliminary measurements were based on the weight gain of these filters (5 - 8 mg), but this procedure proved to be in error tending to be on the low side. The final procedure used for concentration determination involved collecting samples on filters and determining the phthalate mass by extraction and GC analysis.

To the 25-liter per minute aerosol stream was added 0.2 liter per minute of propane to serve as a tracer gas for dilution measurements. The aerosol concentration itself was also monitored using a Sinclair-Phoenix type forward light scattering photometer. Once the impinger output level in terms of mg/cu m was known, this stream was added to the main line of the vapor dilution system (Refer to Butyl Acetate S47 Backup Data Report) and the air flow was adjusted until the desired dilution to 10 mg/cu m was achieved.

For the final di-2-ethylhexyl phthalate data detailed in this report, the Royco/impinger output level was 272 mg/cu m, and this was diluted 25:1 to give a 2S concentration of 10.9 mg/cu m. Both the FID propane monitor and the aerosol photometer showed the same dilution ratios between the generator and 2S values. However, the FID and aerosol photometer did not show the same relative ratios through the small 0.5S and 1S orifices of the dilution system. The dilutions as determined by the FID/Propane and the aerosol photometer were as follows:

Concentration Level	0.5S	1S	2S
FID Ratio	0.240	0.490	1.000
Aerosol Photometer Ratio	0.186	0.450	1.000

The difference is undoubtedly due to aerosol losses through the dilution orifice. The aerosol photometer derived ratios were used as the basis for the known dilutions. Thus, the di-2-ethylhexyl phthalate concentrations at the three test levels were 2.03, 4.90, and 10.9 mg/cu m. All six samples at the three test levels were collected simultaneously at 1.1 liters per minute for 30 minutes (32 liters), at a temperature and pressure of 23°C and 761 mm Hg. The 2S aerosol concentration was monitored throughout the calibration and collection and was observed to remain constant.

The collection efficiency (>99.9%) of the Type AA filter for 0.3 micrometer DOP aerosol is widely documented in the literature and has been confirmed in other studies in the contractor's laboratory. Limited observations also showed no aerosol transmission through the AA filter at the Royco output stream and from the 2S concentration line.

Discussion

Two extraction techniques were tested for optimum sample recovery from glass fiber filters. One approach was an adaptation of the extraction procedure for coal tar pitch volatiles (ASTM Proposed Method). The method consists of transfering the filter to a 15 ml centrifuge tube followed by treating the sample with three successive 3 - 5 ml aliquots of carbon disulfide, ultrasonerating, decanting and concentrating the total extract to 1.0 ml. Using this centrifuge tube technique, the average recovery for samples spiked at concentrations equivalent to 30 liters at the standard level was 48% $\pm$ 12%.

The other technique uses a disposable pipet for the extraction process. The typical pipet used is a Fisher brand disposable pipet modified such that the upper 1-inch portion with the constricting notch is cut off and the lower tapered end is flame-sealed. The modified pipet serves as the extraction tube which holds the rolled filter and the carbon disulfide eluent. The extraction process is aided by the use of an ultrasonic bath for 30 minutes. (A few experiments showed that 15 minutes tended to give greater scatter of data.) The ultrasonic bath used was an Ultrasonics Instrument International Megason Ultrasonic Cleaner Model G-T-120-80-1 with a power rating of 20/480 watts at 110 volts/60 cycles and a frequency of 80 kcs. The details of the analytical procedure are discussed in NIOSH Method S40. The pipet technique yielded a higher average recovery of 73% $\pm$ 6% for sample concentrations equivalent to 30 liters at the standard level when added to glass fiber filters.

The first set of 18 generated samples were collected on glass fiber filters. Using the pipet technique for extraction, the data for these 18 samples gave an average recovery of 79% with a high coefficient of variation, $\overline{CV}_2 = 0.141$.

Subsequent experiments were run using Type AA Millipore filters. Using these MCEF filters, higher recoveries and better precision have been obtained. The experimental results indicated that the preferred route is collection on cellulose membrane filters and extraction using the pipet technique.

There were initial problems in measuring the absolute concentration added to the main sample stream as reflected in the high concentration found for the second and third sets of samples. In running the third set, the GC method for determining the sample stream concentrations was introduced, but this experiment was done after the samples had been collected. Thus the fourth sample set was collected, and the concentration data for this set were at the level needed and have been used for the statistical analysis. Summary data for all three sets of samples are given below:

Set No.	Concentration Range mg/cu m	Recovery	$\overline{CV}_2$
2	4.3, 10, 22	NA	0.0290
3	3.09, 7.47, 16.6	99	0.0279
4	2.03, 4.90, 10.9	107	0.0175

The recovery for set 2 is undetermined because of uncertainties in the actual concentration of the sample line. For sets 3 and 4, the sample concentration has been verified by GC analysis of samples collected at the generator outlet as described in the generation section, but the set 3 calibration data were determined after sample collection. These generator calibration filters were treated in a manner similar to that of the 18 samples except that larger volumes (10 - 25 ml) of carbon disulfide were used for the extraction.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0517 \qquad \overline{CV}_2 = 0.0175 \qquad \overline{CV}_T = 0.0570$$

The average recovery of the generated samples over all levels was

$$107 \pm 6.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Di-2-Ethylhexyl Phthalate S40

Analysis

Level	0.5S		1S			2S		
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
0.074	0.071	95.9	0.149	0.144	96.6	0.298	0.292	98.0
0.074	0.078	105.0	0.149	0.135	90.6	0.298	0.281	94.3
0.074	0.071	95.9	0.149	0.148	99.3	0.298	0.301	101.0
0.074	0.073	98.6	0.149	0.143	96.0	0.298	0.268	89.9
0.074	0.067	90.5	0.149	0.140	94.0	0.298	0.277	93.0
0.074	0.067	90.5	0.149	0.137	91.9	0.298	0.317	106.0
n =		6			6			6
mean		96.1			94.7			97.0
std dev		5.45			3.21			5.86
CV_1		0.0567			0.0339			0.0604

$\overline{CV}_1$ 0.0517

$\overline{CV}_{\overline{A+DE}}$ 0.0558

15081

Data Sheet: Di-2-Ethylhexyl Phthalate S40
Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.072	32.9	2.19	2.03	
	0.069	32.5	2.12	2.03	
	0.072	32.8	2.20	2.03	
	0.070	33.4	2.10	2.03	
	0.070	32.8	2.13	2.03	
	0.068	32.3	2.10	2.03	
		n = 6			
		mean	2.14		105
		std dev	0.0443		
		CV_2	0.0207		
1S	0.170	32.2	5.28	4.90	
	0.172	32.5	5.29	4.90	
	0.172	32.5	5.29	4.90	
	0.173	32.8	5.27	4.90	
	0.174	32.5	5.35	4.90	
	0.175	32.7	5.35	4.90	
		n = 6			
		mean	5.31		108
		std dev	0.0356		
		CV_2	0.0067		
2S	0.402	32.9	12.2	10.9	
	*	*	*	10.9	
	0.384	32.5	11.8	10.9	
	0.394	33.1	11.9	10.9	
	0.395	32.5	12.2	10.9	
	0.378	32.5	11.6	10.9	
		n = 5			
		mean	11.9		109
		std dev	0.261		
		CV_2	0.0219		
		$\overline{CV_2}$	0.0175		

*Lost sample

Backup Data Report

Substance: 2-Ethoxyethyl Acetate, No. S41

OSHA Standard: 540 mg/cu m

Chemical used for validation: 2-Ethoxyethyl Acetate, Aldrich Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S41 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of 2-ethoxyethyl acetate represented in a 10 liter air sample. The charcoal used was LOT 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using dodecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 112.1 mg/min of 2-ethoxyethyl acetate via a syringe injector to a dry air stream flowing at a rate of .1021 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 38 mg of 2-ethoxyethyl acetate when a test atmosphere containing 1098 mg/cu m of 2-ethoxyethyl acetate in air was sampled at 0.19 liters per minute for 182 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV_1} = 0.0236 \qquad \overline{CV_2} = 0.0360 \quad CV_T = 0.0624$$

The average recovery of the generated samples over all levels was

$$109.6 \pm 7.2\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV_2}^2 + (0.07)^2} \left(\frac{100}{\% \text{ Recovery}}\right) 100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: 2-Ethoxyethyl Acetate S41

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.53	1.78	0.704	5.26	4.38	0.833	10.7	9.02	0.843
2.53	1.63	0.644	5.26	4.38	0.833	10.7	9.03	0.844
2.53	1.66	0.656	5.26	4.44	0.844	10.7	9.03	0.844
2.53	1.75	0.692	5.26	4.49	0.854	10.7	9.08	0.849
2.53	1.72	0.680	5.26	4.42	0.840	10.7	8.76	0.819
2.53	1.78	0.704	5.26	4.36	0.829	10.7	9.09	0.850
n =		6			6			6
mean		0.680			0.839			0.842
std dev		0.0252			0.00920			0.0114
CV_1		0.0370			0.0110			0.0135

$\overline{CV}_1$ 0.0236

$\overline{CV}_{A+\overline{DE}}$ 0.0255

Data Sheet: 2-Ethoxyethyl Acetate S41

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.88	2.69	10.0	269	262	103
	1.89	2.70	10.0	270	262	103
	*	-	-	-	-	-
	2.11	3.01	10.0	301	262	115
	2.02	2.89	10.0	289	262	110
	2.13	3.04	10.0	304	262	116
			n = 5			
			mean	287		109
			std dev	16.6		
			CV_2	0.0578		
1S	4.80	5.71	10.0	571	540	106
	4.86	5.79	9.91	584	540	108
	4.64	5.52	9.83	562	540	104
	4.97	5.92	10.2	580	540	107
	4.97	5.92	10.0	592	540	110
	4.72	5.62	9.96	564	540	104
			n = 6			
			mean	576		107
			std dev	11.8		
			CV_2	0.0205		
2S	10.4	12.4	10.3	1200	1100	109
	10.4	12.4	10.0	1240	1100	113
	10.6	12.6	10.0	1260	1100	115
	10.6	12.6	10.0	1260	1100	115
	10.7	12.7	10.4	1220	1100	111
	10.6	12.6	10.0	1260	1100	115
			n = 6			
			mean	1240		113
			std dev	25.3		
			CV_2	0.0204	$\overline{CV}_2$	0.0360

*Sample lost

Backup Data Report

Substance: Methyl Acetate, No. S42

OSHA Standard: 610 mg/cu m

Chemical used for validation: Methyl Acetate, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S42 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methyl acetate represented in a 7.9 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml. vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using decane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of the normal procedure, except for a reduction of sample volume to 7 liters in accordance with breakthrough results.

Generation

Test atmosphere samples at a concentration 4 times the OSHA standard level were generated by delivering 269 mg/min of methyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1028 cu m/min. The three sample lines were then maintained at dilution ratios of 0.1311, 0.2557 and 0.5097 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 35 minutes (7.9 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 13.7 mg of methyl acetate when a test atmosphere containing 1333 mg/cu m of methyl acetate in air was sampled at 0.19 liters per minute for 54 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0159 \qquad \overline{CV}_2 = 0.0212 \qquad CV_T = 0.0547$$

The average recovery of the generated samples over all levels was

$$107.3 \pm 6.8\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^{\,2} + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methyl Acetate S42

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.04	1.76	0.863	4.27	3.78	0.885	8.53	7.84	0.919
2.04	1.78	0.873	4.27	3.87	0.906	8.53	7.71	0.904
2.04	1.73	0.848	4.27	3.86	0.904	8.53	7.71	0.904
2.04	1.69	0.828	4.27	3.89	0.911	8.53	7.60	0.891
2.04	1.78	0.873	4.27	3.77	0.883	8.53	7.80	0.914
2.04	1.76	0.863	4.27	3.91	0.916	8.53	7.78	0.912
n =		6			6			6
mean		0.858			0.901			0.907
std dev		0.0173			0.0137			0.00991
CV_1		0.0202			0.0152			0.0109

$\overline{CV_1}$ 0.0159

$\overline{CV_{A+DE}}$ 0.0172

Data Sheet: Methyl Acetate S42

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.69	3.06	7.88	388	343	113
	2.75	3.13	7.88	397	343	116
	2.74	3.11	7.88	395	343	115
	2.64	3.00	7.88	381	343	111
	2.70	3.07	7.88	390	343	114
	2.81	3.19	7.88	405	343	118
			n = 6			
			mean	393		115
			std dev	8.26		
			CV_2	0.0210		
1S	5.03	5.59	7.88	709	668	106
	5.04	5.60	7.81	717	668	107
	5.24	5.82	7.74	752	668	113
	5.29	5.88	8.02	733	668	110
	5.14	5.71	7.91	722	668	108
	5.02	5.58	7.84	712	668	107
			n = 6			
			mean	724		108
			std dev	16.0		
			CV_2	0.0222		
2S	9.39	10.4	8.12	1280	1330	96.2
	9.17	10.2	7.91	1290	1330	97.0
	9.34	10.5	7.91	1330	1330	100
	9.38	10.4	7.88	1320	1330	99.2
	9.72	10.8	8.19	1320	1330	99.2
	9.53	10.6	7.91	1340	1330	101
			n = 6			
			mean	1313		98.8
			std dev	23.4		
			CV_2	0.0178		$\overline{CV}_2$ 0.0212

Backup Data Report

Substance: Isobutyl Acetate, No. S44

OSHA Standard: 700 mg/cu m

Chemical used for validation: Isobutyl Acetate, Eastman Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S44 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of isobutyl acetate represented in a 10 liter air sample. The charcoal used was LOT 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 131.7 mg/min of isobutyl acetate via a syringe injector to a dry air stream flowing at a rate of .1026 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 27.6 mg of isobutyl acetate when a test atmosphere containing 1284 mg/cu m of isobutyl acetate in air was sampled at 0.19 liters per minute for 113 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV_1} = 0.0161 \qquad \overline{CV_2} = 0.0416 \quad CV_T = 0.0654$$

The average recovery of the generated samples over all levels was

$$102.7 \pm 7.9\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV_2}^2 + (0.07)^2} \left(\frac{100}{\% \text{ Recovery}}\right) \quad 100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Isobutyl Acetate S44

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.50	3.27	0.934	7.00	6.62	0.919	14.0	13.7	0.979
3.50	3.27	0.934	7.00	6.67	0.926	14.0	13.4	0.957
3.50	3.28	0.937	7.00	6.40	0.887	14.0	13.4	0.957
3.50	3.25	0.929	7.00	6.72	0.931	14.0	13.0	0.929
3.50	3.28	0.937	7.00	6.58	0.913	14.0	13.5	0.964
3.50	3.22	0.920	7.00	6.65	0.923	14.0	13.8	0.986
n =		6			6			6
mean		0.932			0.917			0.962
std dev		0.00649			0.0157			0.0200
CV_1		0.00697			0.0171			0.0208

$\overline{CV}_1$ 0.0161

$\overline{CV}_{A+\overline{DE}}$ 0.0173

Data Sheet: Isobutyl Acetate S44

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.08	3.31	10.1	326	306	107
	2.79	3.00	10.1	297	306	97.1
	2.69	2.89	10.1	286	306	93.5
	3.16	3.40	10.1	337	306	110
	3.15	3.39	10.1	336	306	110
	3.15	3.39	10.1	336	306	110
			n = 6			
			mean	320		105
			std dev	22.5		
			CV_2	0.0702		
1S	6.14	6.53	10.1	647	631	103
	6.19	6.59	10.0	659	631	104
	6.20	6.60	9.95	663	631	105
	6.35	6.76	10.3	656	631	104
	6.27	6.67	10.2	654	631	104
	6.24	6.64	10.1	657	631	104
			n = 6			
			mean	656		104
			std dev	5.37		
			CV_2	0.00818		
2S	12.7	13.2	10.1	1310	1280	102
	12.3	12.8	10.2	1250	1280	97.7
	12.5	13.0	10.2	1270	1280	92.2
	12.5	13.0	10.1	1290	1280	101
	12.8	13.3	10.5	1270	1280	99.2
	12.4	12.9	10.2	1260	1280	98.4
			n = 6			
			mean	1275		99.6
			std dev	21.7		
			CV_2	0.0170		$\overline{CV_2}$ 0.0416

Backup Data Report

Substance: Isoamyl Acetate

OSHA Standard: 100 ppm (525 mg/cu m)

Chemical used for validation: Isopentyl Acetate, MC/B Chromatoquality

Procedure

The general procedure used is described in NIOSH Method No. S45 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of isoamyl acetate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using tridecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 89.5 mg/min of isoamyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1024 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 46 minutes (10 liters). This is the second set of 18 samples collected and these data have been used for the statistical analysis. The experiment was repeated because of the low recovery (86%) observed in the first set. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 33 mg of isoamyl acetate when a test atmosphere containing 1010 mg/cu m of isoamyl acetate in air was sampled at 0.19 liters per minute for 170 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough studies were done in conjunction with the first sample set collected.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0101 \qquad \overline{CV}_2 = 0.0241 \quad CV_T = 0.0557$$

The average recovery of the generated samples over all levels was

$$91.4 \pm 8.1\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^{\,2} + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Isoamyl acetate S45

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.60	2.34	0.900	5.20	4.70	0.904	10.4	9.42	0.908
2.60	2.38	0.915	5.20	4.71	0.906	10.4	9.45	0.909
2.60	2.39	0.919	5.20	4.70	0.904	10.4	9.40	0.904
2.60	2.40	0.923	5.20	4.69	0.902	10.4	9.39	0.903
2.60	2.37	0.912	5.20	4.67	0.898	10.4	9.31	0.895
2.60	2.30	0.885	5.20	4.73	0.910	10.4	9.50	0.913
n =		6			6			6
mean		0.909			0.904			0.905
std dev		0.0141			0.00400			0.00622
CV_1		0.0155			0.00442			0.00687

$\overline{CV_1}$ 0.0101

$\overline{CV_{A+\overline{DE}}}$ 0.0109

Data Sheet: Isoamyl Acetate S45

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.77	1.95	10.2	191	208	91.8
	1.81	2.00	10.2	196	208	94.2
	1.79	1.98	10.2	194	208	93.3
	1.68	1.85	10.2	181	208	87.0
	1.81	2.00	10.2	196	208	94.2
	1.81	2.00	10.2	196	208	94.2
			n = 6			
			mean	192		92.3
		standard deviation		5.89		
			CV_2	0.0307		
1S	3.67	4.05	10.2	397	430	92.3
	3.64	4.02	10.1	398	430	92.6
	3.60	3.97	10.0	397	430	92.3
	2.61*	2.88*	10.4*	277*	430	
	3.47	3.83	10.2	375	430	87.2
	3.65	4.03	10.1	399	430	92.8
			n = 5			
			mean	393		91.4
		standard deviation		10.2		
			CV_2	0.0260		
2S	7.19*	7.94*	10.5*	756*	874	
	7.67	8.47	10.2	830	874	95.0
	7.61	8.40	10.2	824	874	94.3
	7.64	8.43	10.2	826	874	94.5
	8.00	8.83	10.6	833	874	95.3
	7.74	8.54	10.2	837	874	95.8
			n = 5			
			mean	830		95.0
		standard deviation		5.24		
			CV_2	0.0063		

*These values excluded from statistical analysis

$\overline{CV}_2$ 0.0241

Backup Data Report

Substance: sec-Butyl Acetate

OSHA Standard: 950 mg/cu m

Chemical used for validation: sec-Butyl Acetate, Eastman reagent grade

Procedure

The general procedure used is described in NIOSH Method No. S46 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of sec-butyl acetate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 205.4 mg/min of sec-butyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1024 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 39 minutes (9 liters). This is the second set of 18 samples collected and these data have been used for the statistical analysis. The data on the first set of 18 samples (see Sampling and Analysis 1) were rejected because three data points appeared to be "outliers". Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 30 mg of sec-butyl acetate when a test atmosphere containing 1800 mg/cu m of sec-butyl acetate in air was sampled at 0.19 liters per minute for 87 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough studies were done in conjunction with the first sample set collected.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0166 \qquad \overline{CV}_2 = 0.0192 \quad CV_T = 0.0540$$

The average recovery of the generated samples over all levels was

$$97.7 \pm 7.4\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^2 + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: sec-Butyl Acetate S46

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.70	4.30	0.915	9.57	8.82	0.922	19.1	18.0	0.942
4.70	4.22	0.898	9.57	8.53	0.891	19.1	18.7	0.979
4.70	4.28	0.911	9.57	8.75	0.914	19.1	18.8	0.984
4.70	4.20	0.894	9.57	8.90	0.930	19.1	18.6	0.974
4.70	4.15	0.883	9.57	8.83	0.923	19.1	18.2	0.953
4.70	4.36	0.928	9.57	8.77	0.916	19.1	18.6	0.974
n =		6			6			6
mean		0.905			0.916			0.968
std dev		0.0162			0.0135			0.0164
CV_1		0.0179			0.0147			0.0170

$\overline{CV}_1$ 0.0166

$\overline{CV}_{A+DE}$ 0.0179

Data Sheet: sec-Butyl Acetate

Sampling and Analysis (1)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.45	4.89	10.1	484	430	113
	4.41	4.85	10.1	480	430	112
	3.96	4.35	10.1	431	430	100
	4.44	4.88	10.1	483	430	112
	4.42	4.86	10.1	481	430	112
	4.38	4.81	10.1	476	430	111
			n = 6			
			mean	473		110
			standard deviation	20.5		
			CV_2	0.0434		
1S	9.07	9.86	10.1	976	886	110
	5.53*	6.01	10.0*	601*	886	67.8
	9.07	9.86	9.95	991	886	112
	5.66*	6.15*	10.3*	597*	886	67.4
	9.07	9.86	10.2	967	886	109
	9.30	10.1	10.1	1000	886	113
			n = 4			
			mean	984		96.5
			standard deviation	14.8		
			CV_2	0.0150		
2S	19.6	20.2	10.4	1940	1800	108
	19.1	19.7	10.2	1930	1800	107
	19.2	19.8	10.2	1940	1800	108
	18.6	19.2	10.1	1900	1800	106
	19.5	20.1	10.6	1900	1800	106
	16.1*	16.6*	10.2*	1627*	1800	90.4
			n = 5			
			mean	1920		104
			standard deviation	20.5		
			CV_2	0.0107	$\overline{CV}_2$	0.0297

*These values excluded from statistical analysis

Data Sheet: sec-Butyl Acetate S46

Sampling and Analysis (2)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.73	4.19	8.63	486	478	102
	3.56	4.00	8.63	463	478	96.9
	3.82	4.29	8.63	497	478	104
	3.64	4.09	8.63	474	478	99.2
	3.73	4.19	8.63	486	478	102
	3.69	4.15	8.63	481	478	101
			n = 6			
			mean	481		101
			standard deviation	11.7		
			CV_2	0.0242		
1S	7.59	8.34	8.63	966	986	98.0
	7.48	8.22	8.55	961	986	97.5
	7.59	8.34	8.48	983	986	99.7
	7.69	8.45	8.79	961	986	97.5
	7.71	8.47	8.67	977	986	99.1
	3.16*	3.55*	8.59*	413*	986	
			n = 5			
			mean	970		98.4
			standard deviation	9.94		
			CV_2	0.0102		
2S	15.8	16.6	8.90	1865	2005	93.0
	15.2	16.0	8.67	1845	2005	92.0
	15.6	16.4	8.67	1890	2005	94.3
	15.5	16.3	8.63	1890	2005	94.3
	15.8	16.6	8.53	1950	2005	97.3
	15.4	16.2	8.67	1870	2005	93.3
			n = 6			
			mean	1885		94.0
			standard deviation	36.1		
			CV_2	0.0192		$\overline{CV}_2$ 0.0192

* These values excluded from statistical analysis

Backup Data Report

Substance: Butyl Acetate, No. S47

OSHA Standard: 150 ppm (710 mg/cu m)

Chemical used for validation: Butyl Acetate, Eastman Spectro Grade

Procedure

The general procedure used is described in NIOSH Method No. S47 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of butyl acetate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using dodecane as internal standard. Details of the analysis procedures may be found in this Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 150.9 mg/min of butyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1023 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in this Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 30.3 mg of butyl acetate when a test atmosphere containing 1475 mg/cu m of butyl acetate in air was sampled at 0.19 liters per minute for 108 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0204 \qquad \overline{CV}_2 = 0.0469 \qquad CV_T = 0.0690$$

The average recovery of the generated samples over all levels was

$$99.9 \pm 8.4\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^2 + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right) 100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Butyl Acetate S47

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.53	3.43	0.972	7.06	6.53	0.925	14.1	13.1	0.929
3.53	3.25	0.921	7.06	6.72	0.952	14.1	13.3	0.943
3.53	3.25	0.921	7.06	6.68	0.946	14.1	13.3	0.943
3.53	3.31	0.938	7.06	6.47	0.916	14.1	13.2	0.936
3.53	3.29	0.932	7.06	6.76	0.958	14.1	13.0	0.922
3.53	3.48	0.986	7.06	6.70	0.949	14.1	13.3	0.943

n =	6	6	6
mean	0.945	0.941	0.936
std dev	0.0275	0.0166	0.00885
CV_1	0.0291	0.0177	0.00946

$\overline{CV}_1$ 0.0204

$\overline{CV}_{A+\overline{DE}}$ 0.0220

Data Sheet: Butyl Acetate S47

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.36	3.61	10.0	361	352	103
	3.36	3.61	10.0	361	352	103
	3.07	3.30	10.0	330	352	93.8
	3.40	3.66	10.0	366	352	104
	2.90	3.12	10.0	312	352	88.6
	3.45	3.71	10.0	371	352	105
			n = 6			
			mean	350		99.6
			std dev	23.6		
			CV_2	0.0674		
1S	6.70	7.13	10.0	713	725	98.3
	6.84	7.28	9.93	733	725	101
	6.82	7.26	9.85	737	725	102
	6.90	7.34	10.2	720	725	99.3
	6.93	7.37	10.1	729	725	100
	6.88	7.32	9.98	733	725	101
			n = 6			
			mean	728		100
			std dev	9.16		
			CV_2	0.0126		
2S	13.9	14.8	10.3	1440	1480	97.3
	13.2	14.0	10.1	1390	1480	93.9
	14.7	15.6	10.1	1540	1480	104
	14.5	15.4	10.0	1540	1480	104
	14.1	15.0	10.4	1440	1480	97.3
	14.6	15.5	10.1	1530	1480	103
			n = 6			
			mean	1480		99.9
			std dev	64.8		
			CV_2	0.0438		$\overline{CV}_2$ 0.0469

Attachment to Butyl Acetate S47 Backup Data Report

VAPOR GENERATION/DILUTION SYSTEM

The vapor generation/dilution system used for the validation studies of Butyl Acetate and several other vapors and gases is shown schematically in Figure 1. The system basically consists of a main line air stream to which are added predetermined amounts of various liquids, gases or aerosols to generate the desired vapor concentrations. From the main line, three dilution arms branch off in which the desired multiples 0.5, 1.0 and 2.0 times the OSHA Standard concentration level are established. Six charcoal tubes are connected in parallel to each of the three dilution lines and are connected via critical flow orifices (CFO's) to the three corresponding vacuum lines.

Air flow rates through the system are established by means of critical flow orifices (CFO's) and flow restrictors. The primary air system derived from the house air compressor is maintained at 20.0 psig. The appropriate orifice diameters are chosen to maintain an air flow of approximately 0.1 cu m/min in the Main Line and an addition of 0.05 cu m/min to each of the dilution lines. The main line is maintained at 8 cm H_2O pressure by means of a needle valve. Appropriate flow restrictor diameters are chosen for the 0.5S, 1S and 2S dilution lines so as to give the desired final concentrations of vapor in air.

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 cu m/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.17 and 0.050 cu m/min respectively of the Main Line concentration added to the dilution air, thus giving the desired final concentrations. Where a Main Line concentration of 2X the OSHA Standard is generated, no dilution air is added to the 2S dilution line -- 0.017 cu m/min is simply allowed to flow through this line -- and 0.050 cu m/min of dilution air is added to the 0.050 cu m/min and 0.017 cu m/min of Main Line mixture admitted to the 1S and 0.5S dilution lines, respectively.

All materials which the vapor may contact before collection are 316 or 304 stainless steel. A glass heater is included where the liquids are added to the main line. Shutoff ball valves are placed in the dilution lines to allow their independent operation and the calibration of air flows. The Main Line has a 2.54 cm (1 in) OD, and the dilution lines are 1.90 cm (0.75 in) OD. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

Vapor Generation

Vapor concentrations are generated by adding known amounts of liquid to the Main Line continuously at fixed rates using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25G needle in the Main Line by a short length of 0.16 cm (1/16 in) OD Teflon tubing. The 25G

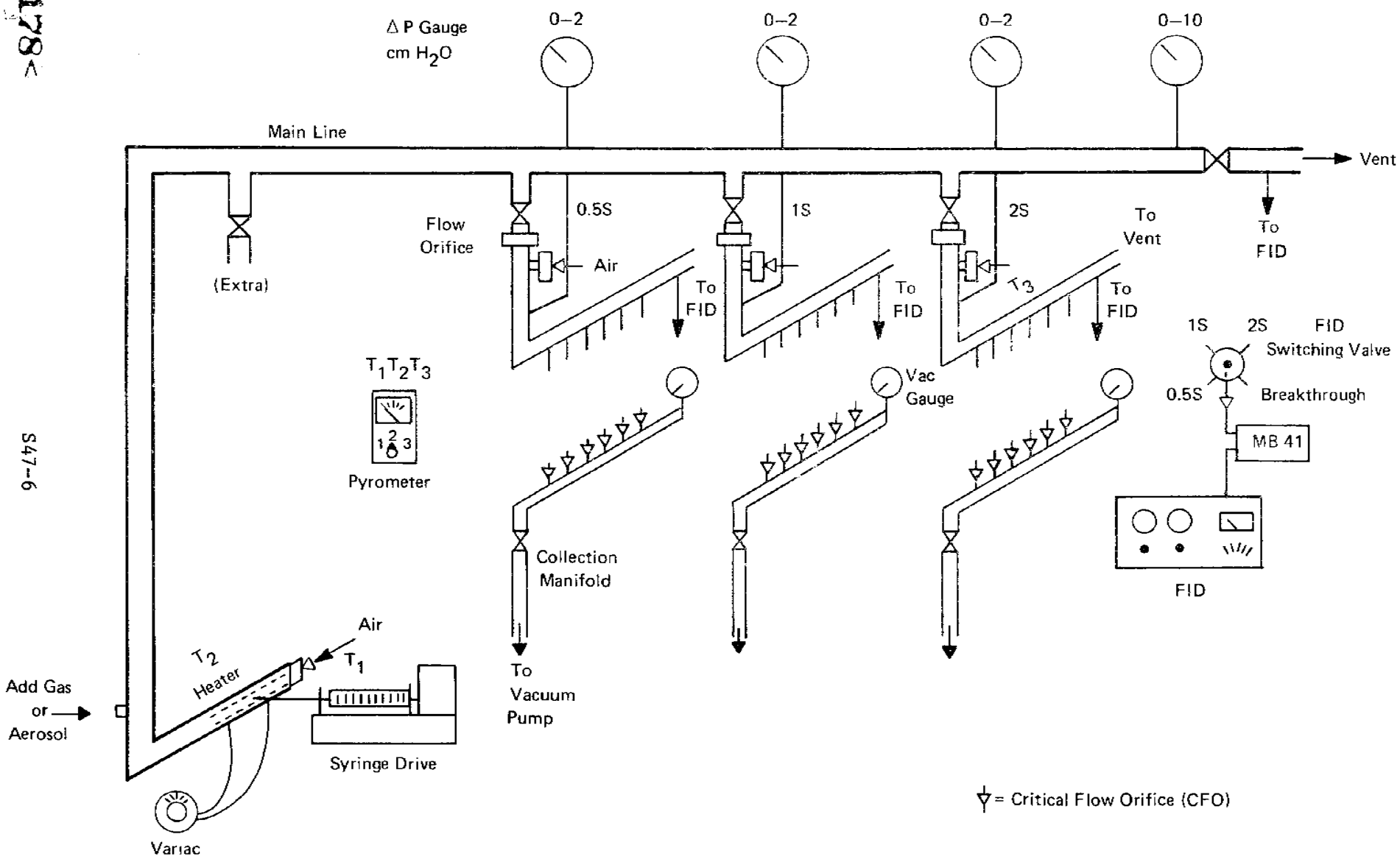


FIGURE 1 VAPOR GENERATION/DILUTION SYSTEM

needle is mounted such that the tip of the needle rests inside a 10 cm length of 8 mm glass tubing wound with resistance wire. The appropriate amount of current is applied to the heater to assure steady and complete vaporization of the liquid.

Air Supply

Air from the house compressor is treated by passing it sequentially through a cotton filter, a silica gel bed, a charcoal bed and a high efficiency glass fiber filter for removal of water, hydrocarbons and particulate. This air is then connected to a manifold containing six takeoff ball valves. The pressure (20 psig) at the manifold is maintained with a Nullmatic Moore 40H50 regulator and monitored with an Ashcroft 0-60 psig test gauge. The air supply is used for each of the dilution system connections as well as for the flame ionization detector monitor flame and "zero" air.

Sample Collection Manifold

Sample flow through the charcoal tubes connected to the dilution lines is established by connecting each of the tubes by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) OD vacuum manifold. Each dilution line has a separate manifold which derives its vacuum from a Model 0322 Gast vacuum pump. The orifices are jewel orifices pressed into threaded Teflon rod. One end of the rod is screwed into a tee on the manifold, and the other has a hose tabulation fitting connected to it. The orifice is protected from plugging by means of a piece of 100 mesh stainless steel screen.

Vent System

All excess vapor-laden air is collected via a 3.81 cm (1 1/2 in) PVC manifolding system where it is passed through a 0.3 x 0.3 x 0.6 M charcoal bed. Flow is established by means of a pressure blower on the exit side of the charcoal bed, and it is vented to the laboratory hood exhaust.

Calibration

Syringe Drive

Preliminary calibrations have been conducted so that the approximate delivery rates of the syringe drive are known at each setting for several syringe sizes. These values are used to set the approximate delivery rate for the specific liquid. The syringe is then filled and connected to a weighing bottle, and the drive is activated for a period of time to allow the actual delivery rate to be determined in mg/min by weighing the amount collected. Sufficient time is allowed to provide a weight change which can be measured reliably and thus enable a precise calibration. Usually 0.2 - 5 g is collected depending on the specific compound being studied.

Air Flows

Main Line -- The air flow delivered by the Main Line CFO was determined by measurement with a Singer Dry Test Meter. The meter had previously been calibrated with a spirometer primary standard. Using the 0.310 cm diameter orifice at 20 psig air pressure, the flow was found to be 0.1041 cu m/min corrected to 25°C and 760 mm Hg.

Dilution Lines -- The air flow through each of the dilution line CFO's and restrictor orifices was similarly measured with the Dry Test Meter to assure that they met design parameters, but these values did not provide the primary basis for determination of vapor concentration.

Collection CFO's -- Since the flow rate through the sample collection CFO's was lower (0.2 and 1.0 liter per minute) than appropriate for use with the Dry Test Meter, the flow rate of each of these orifices was measured using an SKC soap bubble meter which was independently calibrated by gravimetrically measuring water capacity.

All volume measurements have been referenced to normal temperature and pressure of 25°C and 760 mm Hg.

Calculation of Vapor Concentration

The concentration of the vapor in the main line is calculated from the calibrated syringe delivery rate, mg/min, and the Main Line air flow rate, cu m/min. Thus these two values each of which can be determined reliably, yield the Main Line concentration directly in the desired units, mg/cu m.

Dilution Ratios

The concentration of vapor in the dilution lines is determined from the concentration calculated in the Main Line and the dilution ratio determined between the dilution lines and the main line. These dilution ratios were measured by adding a controlled amount of propane gas to the Main Line and then measuring the relative concentration in each of the lines using a Beckman Model 402 heated hydrocarbon analyzer. The procedure was repeated several times and is regularly checked during the program.

In the case where 4X or 2X concentration level conditions were generated, the dilution ratios reported below were observed.

		Relative Concentration		
Case Generated	Main Line	2S	1S	0.5S
4X	1.000	0.5097	0.2557	0.1311
2X	1.000	1.000	1.4916	0.2384

Each of these sets of values represents a different set of air flow and orifice selection conditions as previously discussed. Point to point comparison of the six sample ports on each manifold showed less than a 1% variation in concentration among them.

Monitors

To provide a ready check on operating conditions, several gauges or monitors have been included in the system. Dwyer Magnehelic gauges monitor the pressure on the Main Line and each of the dilution lines. A 0-10 cm H_2O gauge is used on the Main Line (Setpoint 8 cm) and 0-2 cm H_2O gauges are used for the dilution lines. The purpose of these latter gauges is to provide a check against possible back pressure developing in these lines which would affect the dilution ratios.

The flame ionization detector (FID) is used to determine the time at which the Main Line concentration has reached equilibrium and to monitor the concentration level during breakthrough studies and sample collection.

Breakthrough Studies

For the measurement of charcoal tube capacity for a given vapor (breakthrough) six charcoal tubes containing only the 100 mg "front half" section of charcoal are connected in parallel to the 2S dilution line and to a 0.635 cm (1/4 in) OD stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp Model MB41 pump. Flow through the orifice was measured as 1.14 liters per minute providing a 0.19 liter per minute flow to each of the tubes. Equal flow through each of the tubes is insured by carefully selecting and/or adjusting packing in the tubes to have an equal pressure drop when precalibrated at a 0.2 liter per minute flow rate.

Once a steady state vapor concentration is established, the 2S concentration level is used to set the 100% point on the hydrocarbon analyzer. Then the valve is switched, and the flow from the breakthrough manifold is passed through the hydrocarbon analyzer and monitored either until 5% of the 2S level is observed or for a period of four hours -- whichever occurs first.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.
2. Syringe delivery rate is calibrated
3. Liquid is fed until vapor concentration equilibrium is established.
4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.
5. The six sets of samples from the three concentration levels are collected simultaneously.

Backup Data Report

Substance: n-Propyl acetate, No. S48

OSHA Standard: 840 mg/cu m

Chemical used for validation: Propyl Acetate, Eastman Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S48 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of n-propyl acetate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the pre-packed SKC breakthrough tubes containing only the 100 mg front section of charcoal. Gas chromatographic analyses were done with the Varian Model 8000 automatic sample injector using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 164 mg/min of n-propyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.102 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 28.7 mg of n-propyl acetate when a test atmosphere containing 1609 mg/cu m of n-propyl acetate in air was sampled at 0.19 liters per minute for 94 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0180 \qquad \overline{CV}_2 = 0.0250 \qquad CV_T = 0.0563$$

The average recovery of the generated samples over all levels was

$$106.8 \pm 7\%$$

The uncertainty in this value was computed from

$$\sqrt{\overline{CV}_2^{\,2} + (0.07)^2}\left(\frac{100}{\%\ \text{Recovery}}\right)100$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Propyl Acetate S48

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.18	3.88	0.928	8.44	7.69	0.911	16.9	16.2	0.959
4.18	3.83	0.916	8.44	7.91	0.937	16.9	15.6	0.924
4.18	3.80	0.909	8.44	8.05	0.954	16.9	16.3	0.964
4.18	3.94	0.943	8.44	7.96	0.943	16.9	15.8	0.935
4.18	3.84	0.919	8.44	8.15	0.966	16.9	16.0	0.947
4.18	3.80	0.909	8.44	7.73	0.916	16.9	15.7	0.929
n =		6			6			6
mean		0.921			0.938			0.943
std dev		0.0130			0.0213			0.0166
CV_1		0.0142			0.0227			0.0176

$\overline{CV}_1$ 0.0180

$\overline{CV}_{A+\overline{DE}}$ 0.0194

Data Sheet: Propyl Acetate S48

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.96	4.30	10.0	430	384	112
	3.94	4.28	10.0	428	384	111
	3.96	4.30	10.0	430	384	112
	3.92	4.26	10.0	426	384	111
	3.90	4.24	10.0	424	384	110
	3.94	4.28	10.0	428	384	111
			n = 6			
			mean	428		111
			std dev	2.34		
			CV_2	0.00546		
1S	7.83	8.33	9.99	834	791	105
	7.92	8.43	9.90	852	791	108
	8.00	8.51	9.82	867	791	110
	8.16	8.68	10.2	851	791	108
	8.04	8.55	10.0	855	791	108
	8.00	8.51	9.95	855	791	108
			n = 6			
			mean	852		108
			std dev	10.7		
			CV_2	0.0125		
2S	16.1	17.1	10.3	1660	1610	103
	14.1	15.0	10.0	1500	1610	93.2
	15.8	16.8	10.0	1680	1610	104
	15.6	16.6	10.0	1660	1610	103
	16.2	17.2	10.4	1650	1610	102
	15.6	16.6	10.0	1660	1610	103
			n = 6			
			mean	1635		101
			std dev	66.9		
			CV_2	0.0409	$\overline{CV}_2$	0.0250

Backup Data Report

Substance: Ethyl Acetate

OSHA Standard: 1400 mg/cu m

Chemical used for validation: Ethyl Acetate, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S49 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of ethyl acetate represented in a 6 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127. The sample size was reduced to 6 liters in accordance with breakthrough results.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 306.7 mg/min of ethyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1039 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 27 minutes (6 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 25 mg of ethyl acetate when a test atmosphere containing 2950 mg/cu m of ethyl acetate in air was sampled at 0.19 liters per minute for 45 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.00762 \qquad \overline{CV}_2 = 0.0283 \qquad \overline{CV}_T = 0.0575$$

The average recovery of the generated samples over all levels was

$$97.9 \pm 7.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Ethyl Acetate S49

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.15	3.71	0.894	8.11	7.18	0.885	16.2	14.8	0.914
4.15	3.73	0.899	8.11	7.12	0.878	16.2	14.7	0.907
4.15	3.72	0.896	8.11	7.25	0.894	16.2	14.6	0.901
4.15	3.65	0.880	8.11	7.14	0.880	16.2	14.7	0.907
4.15	3.66	0.882	8.11	7.09	0.874	16.2	14.7	0.907
4.15	3.73	0.899	8.11	7.13	0.879	16.2	14.7	0.907

n =	6	6	6
mean	0.892	0.882	0.907
std dev	0.00850	0.00700	0.00412
CV_1	0.00953	0.00794	0.0045

$\overline{CV_1}$ 0.00762

$\overline{CV_{A+\overline{DE}}}$ 0.00823

Data Sheet: Ethyl Acetate S49
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.72	4.23	6.06	698	704	
	3.54	4.02	6.06	663	704	
	3.81	4.33	6.06	715	704	
	3.56	4.05	6.06	668	704	
	3.81	4.33	6.06	715	704	
	3.79	4.31	6.06	711	704	
			n = 6			
			mean	695		98.7
			std dev	23.7		
			CV_2	0.0342		
1S	7.74	8.80	6.06	1450	1450	
	7.40	8.41	6.01	1400	1450	
	7.59	8.63	5.96	1450	1450	
	7.82	8.89	6.17	1440	1450	
	7.46	8.48	6.09	1390	1450	
	7.68	8.73	6.04	1450	1450	
			n = 6			
			mean	1430		98.6
			std dev	27.6		
			CV_2	0.0193		
2S	16.0	17.6	6.25	2820	2950	
	15.9	17.5	6.09	2870	2950	
	14.9	16.4	6.09	2690	2950	
	16.0	17.6	6.06	2900	2950	
	16.7	18.4	6.30	2920	2950	
	15.9	17.5	6.09	2870	2950	
			n = 6			
			mean	2845		96.4
			std dev	83.1		
			CV_2	0.0292		
			$\overline{CV_2}$	0.0283		

Backup Data Report

Substance: Isopropyl Acetate

OSHA Standard: 250 ppm (950 mg/cu m)

Chemical used for validation: Isopropyl Acetate, Eastman reagent grade

Procedure

The general procedure used is described in NIOSH Method No. S50 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of isopropyl acetate represented in an 8 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127. The sample size was reduced to 8 liters in accordance with breakthrough results.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 191.8 mg/min of isopropyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1024 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 37 minutes (8 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 26 mg of isopropyl acetate when a test atmosphere containing 1870 mg/cu m of isopropyl acetate in air was sampled at 0.19 liters per minute for 72 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.00696 \qquad \overline{CV}_2 = 0.0444 \qquad \overline{CV}_T = 0.0669$$

The average recovery of the generated samples over all levels was

$$103.9 \pm 8.0\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Isopropyl Acetate S50

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.75	3.14	0.837	7.68	6.63	0.863	15.4	13.7	0.890
3.75	3.17	0.845	7.68	6.57	0.855	15.4	13.7	0.890
3.75	3.10	0.827	7.68	6.56	0.854	15.4	13.6	0.883
3.75	3.16	0.843	7.68	6.55	0.853	15.4	13.7	0.890
3.75	3.19	0.851	7.68	6.58	0.857	15.4	13.7	0.890
3.75	3.16	0.843	7.68	6.64	0.865	15.4	13.6	0.883
n =		6			6			6
mean		0.841			0.858			0.888
std dev		0.00820			0.00500			0.00361
CV_1		0.00975			0.00582			0.00407

$\overline{CV_1}$ 0.00696

$\overline{CV_{A+DE}}$ 0.00752

Data Sheet: Isopropyl Acetate S50
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.45*	1.89*	8.19*	231*	446	
	2.94	3.53	8.19	431	446	
	3.24	3.86	8.19	471	446	
	3.35	3.99	8.19	487	446	
	3.36	4.00	8.19	488	446	
	3.35	3.99	8.19	487	446	
			n = 5			
			mean	473		106
			std dev	24.4		
			CV_2	0.0516		
1S	6.35	7.30	8.19	891	920	
	6.86	7.86	8.12	968	920	
	6.41	7.37	8.04	917	920	
	6.02	6.94	8.34	832	920	
	6.65	7.63	8.23	927	920	
	6.85	7.85	8.15	963	920	
			n = 6			
			mean	916		99.6
			std dev	50.4		
			CV_2	0.0551		
2S	15.1	17.0	8.45	2010	1870	
	14.6	16.4	8.23	1990	1870	
	14.7	16.5	8.23	2000	1870	
	14.1	15.7	8.19	1920	1870	
	15.3	17.2	8.52	2020	1870	
	14.8	16.6	8.23	2020	1870	
			n = 6			
			mean	1990		106
			std dev	37.8		
			CV_2	0.0190		
			$\overline{CV}_2$	0.0444		

*These values excluded from statistical analysis

Backup Data Report

Substance: n-Amyl Acetate

OSHA Standard: 525 mg/cu m

Chemical used for validation: n-Amyl Acetate, Ladd Research Industries Analytical Reagent

Procedure

The general procedure used is described in NIOSH Method No. S51 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of n-amyl acetate represented in a 10 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using tridecane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 89.5 mg/min of n-amyl acetate via a syringe injector to a dry air stream flowing at a rate of 0.1028 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 50 minutes (11 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 30 mg of n-amyl acetate when a test atmosphere containing 871 mg/cu m of n-amyl acetate in air was sampled at 0.19 liters per minute for 180 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0189 \qquad \overline{CV}_2 = 0.0066 \qquad \overline{CV}_T = 0.0510$$

The average recovery of the generated samples over all levels was

$$100.5 \pm 7.0\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: n-Amyl Acetate S51

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.63	2.14	0.814	5.25	4.50	0.857	10.5	9.27	0.883
2.63	2.14	0.814	5.25	4.49	0.855	10.5	9.43	0.898
2.63	2.20	0.837	5.25	4.64	0.884	10.5	9.31	0.887
2.63	2.23	0.848	5.25	4.69	0.893	10.5	9.14	0.870
2.63	2.27	0.863	5.25	4.63	0.892	10.5	9.23	0.879
2.63	2.22	0.844	5.25	4.70	0.895	10.5	9.37	0.892
	n = 6			n = 6			n = 6	
	mean	0.837			0.878			0.885
	std dev	0.0195			0.0175			0.0099
	CV_1	0.0233			0.0200			0.0111
				$\overline{CV}_1$	0.0189			
				$\overline{CV}_{A+\overline{DE}}$	0.0204			

Data Sheet: n-Amyl Acetate S51

Sampling and Analysis

Test Level

	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.96	2.36	11.2	211	208	
	1.98	2.39	11.2	213	208	
	1.97	2.37	11.2	212	208	
	1,98	2.39	11.2	213	208	
	1.69*	2.06*	11.2	184*	208	
	1.99	2.40	11.2	214	208	
			n = 5			
			mean	213		102.4
			std dev	1.14		
			CV_2	0.00535		
1S	4.10	4.71	11.2	421	428	
	4.09	4.70	11.1	423	428	
	4.08	4.69	11.0	426	428	
	4.12	4.74	11.4	416	428	
	4.14	4.76	11.2	425	428	
	4.11	4.72	11.1	425	428	
			n = 6			
			mean	423		98.8
			std dev	3.72		
			CV_2	0.00879		
2S	8.95	10.10	11.5	878	871	
	6.65*	7.51*	11.2	671*	871	
	8.71	9.79	11.2	874	871	
	8.68	9.75	11.2	871	871	
	8.96	10.10	11.6	871	871	
	8.66	9.73	11.2	869	871	
			n = 5			
			mean	873		100.2
			std dev	3.51		
			CV_2	0.00402		
			$\overline{CV}_2$	0.00660		

* These values excluded from statistical analysis

BACKUP DATA REPORT

Substance:	Allyl Alcohol, No. S52
OSHA Standard:	2 ppm (4.75 mg/cu m)
Chemical used for validation:	2-Propen-1-ol, 99% Chemical Samples Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 12 mg/ml solution of allyl alcohol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 5% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-dodecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels were not in the proper order and differed by less than one standard deviation. Therefore, the average desorption efficiency for all three levels was used.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 26 percent at the OSHA standard level. Addition of 5 percent of 2-propanol raised the desorption efficiency to 90 percent.

Generation

The test atmosphere was generated by a vapor saturation technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2, nitrogen flow through the saturator was 14 ml/min with the allyl alcohol at a temperature of 0 C. The total gas flow rate of the first stage was 23.1 liters per minute. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube. Concentrations calculated from

air flow and nitrogen flow through the saturator agreed with gas chromatographic analysis of the diluted atmosphere within less than 5 percent.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 8 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Because of the low level it was not possible to monitor the effluent. Therefore, normal charcoal tubes were used and both the front and back sections were analyzed. With a 4-hour sampling period, none of the back sections contained any allyl alcohol. Thus the capacity of this lot of charcoal exceeds 0.38 mg of allyl alcohol and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

Bartlett's test (Reference 3) for homogeneity of variance gave a chi squared value of 12.820, indicating that the hypothesis of equal variance can be rejected at a probability less than 0.01. However, the data for allyl alcohol show acceptable precision. Therefore pooling should not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference 4.

$$\overline{CV}_1 = 0.0226 \qquad \overline{CV}_2 = 0.0995 \qquad \overline{CV}_T = 0.1112$$

The average recovery of the generated samples over all levels was:

98.8%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Backup Data Report for Propylene Oxide, No. S75, ibid.
4. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Allyl Alcohol S52

Analysis

Level	0.5S			1S			2S		
	Added	Found	DE	Added	Found	DE	Added	Found	DE
	0.0240	0.0211	0.880	0.0480	0.0443	0.922	0.0960	0.0870	0.906
	0.0240	0.0199	0.827	0.0480	0.0445	0.927	0.0960	0.0859	0.895
	0.0240	0.0205	0.856	0.0480	0.0449	0.935	0.0960	0.0881	0.917
	0.0240	0.0122	(0.507)*	0.0480	0.0452	0.942	0.0960	0.0866	0.902
	0.0240	0.0219	0.914	0.0480	0.0431	0.899	0.0960	0.0870	0.906
	0.0240	0.0210	0.875	0.0480	0.0439	0.915	0.0960	0.0870	0.906
n =		5			6			6	
mean		0.870			0.923			0.905	
std dev		0.032			0.0154			0.0073	
CV_1		0.0368			0.0166			0.0081	

$\overline{CV}_1$ 0.0226

$\overline{CV}_{A+\overline{DE}}$ 0.0263

*Value deleted as outlier.

Data Sheet: Allyl Alcohol S52

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.0168	0.0187	9.60	1.952	1.800	108.5
	0.0153	0.0171	9.60	1.776	1.800	98.7
	0.0160	0.0178	9.25	1.919	1.800	106.6
	0.0119	0.0132	9.60	1.379	1.800	76.6
	0.0151	0.0168	8.90	1.891	1.800	105.0
	0.0154	0.0171	9.40	1.821	1.800	101.2
			n = 6			
			mean	1.79		99.4
			std dev	0.211		
			CV_2	0.1180		
1S	0.0316	0.0351	9.15	3.836	4.000	95.9
	0.0382	0.0425	10.25	4.145	4.000	103.6
	0.0294	0.0327	10.05	3.255	4.000	81.4
	0.0352	0.0392	9.10	4.303	4.000	107.6
	0.0277	0.0308	9.55	3.226	4.000	80.7
	0.0341	0.0379	9.10	4.167	4.000	104.2
			n = 6			
			mean	3.82		95.6
			std dev	0.476		
			CV_2	0.1245		
2S	0.0829	0.0922	10.85	8.494	8.400	101.1
	0.0760	0.0845	9.70	8.714	8.400	103.7
	0.0718	0.0798	9.40	8.494	8.400	101.1
	0.0736	0.0819	9.30	8.805	8.400	104.8
	0.0775	0.0862	10.15	8.497	8.400	101.2
	0.0768	0.0854	9.85	8.673	8.400	103.3
			n = 6			
			mean	8.61		102.5
			std dev	0.136		
			CV_2	0.0158	$\overline{CV}_2$	0.0995

BACKUP DATA REPORT

Substance:	sec-Butyl Alcohol, No. S53
OSHA Standard:	150 ppm (455 mg/cu m)
Chemical used for validation:	2-Butanol, 99% Chemical Samples Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat sec-butyl alcohol injected with a 10-µl microliter syringe. The amount added was 2.8, 5.6, and 11.2 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-Propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-undecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 82.7 percent. Addition of 1 percent of 2-propanol raised the desorption efficiency to 02.1 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 26.6 liters per minute, and the rate of sec-butyl alcohol injection was 1.35 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 823 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 1 hour, 15 minutes. Thus the capacity of this lot of charcoal is 12.3 mg of sec-butyl alcohol and at the recommended sampling rate, the breakthrough volume is 15 liters. This meets the above requirement.

Precision and Accuracy

Bartlett's test (Reference 3) for homogeneity of variance gave a chi squared value of 11.776, indicating that the hypothesis of equal variance can be rejected at a probability less than 0.01. However, the data for sec-butyl alcohol show excellent precision. Therefore pooling should not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference 4.

$$\overline{CV}_1 = 0.0282 \qquad \overline{CV}_2 = 0.0429 \qquad \overline{CV}_T = 0.0660$$

The average recovery of the generated samples over all levels was:

107.2%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Backup Data Report for Propylene Oxide, No. S75, ibid.
4. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: sec-Butyl Alcohol S53

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
2.250	2.060	0.916	4.500	4.210	0.936	9.000	8.117	0.902
2.250	2.048	0.910	4.500	4.106	0.912	9.000	8.034	0.893
2.250	2.129	0.946	4.500	4.425	0.983	9.000	8.207	0.912
2.250	2.135	0.949	4.500	4.192	0.932	9.000	8.473	0.941
2.250	2.142	0.952	4.500	4.283	0.952	9.000	8.205	0.912
2.250	1.959	0.871	4.500	4.088	0.909	9.000	8.280	0.920
n =		6			6			6
mean		0.924			0.937			0.913
std dev		0.0317			0.0276			0.0167
CV_1		0.0343			0.0295			0.0183

$\overline{CV_1}$ 0.0282

$\overline{CV_{A+DE}}$ 0.0304

Data Sheet: sec-Butyl Alcohol S53

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.595	2.806	9.35	300	271	110.8
	2.576	2.786	9.50	293	271	108.2
	2.509	2.713	9.20	295	271	108.8
	2.597	2.809	9.50	296	271	109.1
	2.414	2.611	8.85	295	271	108.9
	2.459	2.659	9.30	286	271	105.5
			n = 6			
			mean	294.2		108.5
			std dev	4.7		
			CV_2	0.0158		
1S	4.323	4.676	8.95	522	509	102.6
	4.865	5.261	10.15	518	509	101.8
	4.589	4.963	9.95	499	509	98.0
	4.399	4.757	9.05	526	509	103.3
	4.530	4.899	9.30	527	509	103.5
	4.326	4.678	9.05	517	509	101.6
			n = 6			
			mean	518.2		101.8
			std dev	10.3		
			CV_2	0.0198		
2S	7.691	8.318	9.85	844	851	99.2
	8.138	8.801	8.85	994	851	116.9
	7.978	8.628	9.25	933	851	109.6
	7.950	8.598	9.20	935	851	109.8
	8.706	9.415	9.00	1040	851	122.2
	8.388	9.072	9.65	940	851	110.5
			n = 6			
			mean	947.8		111.4
			std dev	66.2		
			CV_2	0.0698	$\overline{CV}_2$	0.0429

BACKUP DATA REPORT

Substance:	Cyclohexanol, No. S54
OSHA Standard:	50 ppm (205 mg/cu m)
Chemical used for validation:	Cyclohexanol, Chromatoquality Matheson, Coleman and Bell

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 500 mg/ml solution of cyclohexanol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 5% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-pentadecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels were not in the proper order and differed by less than one standard deviation, therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 68.7 percent. Addition of 5 percent of 2-propanol raised the desorption efficiency to 93.5 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of cyclohexanol injection was 0.61 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 414 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration was less than 2 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 19.8 mg of cyclohexanol and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV_1} = 0.0154 \qquad \overline{CV_2} = 0.0620 \qquad \overline{CV_T} = 0.0796$$

The average recovery of the generated samples over all levels was:

98.9%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

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Data Sheet: Cyclohexanol S54

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.000	0.981	0.981	2.000	2.020	1.010	4.000	3.860	0.965
1.000	1.002	1.002	2.000	1.964	0.982	4.000	3.965	0.991
1.000	0.997	0.997	2.000	1.961	0.981	4.000	3.959	0.990
1.000	0.968	0.968	2.000	1.936	0.968	4.000	3.897	0.974
1.000	1.007	1.007	2.000	2.000	1.000	4.000	3.877	0.969
1.000	0.970	0.970	2.000	1.987	0.993	4.000	3.994	0.999
n =		6			6			6
mean		0.987			0.989			0.981
std dev		0.0168			0.0151			0.0137
CV_1		0.0170			0.0153			0.0139

CV_1 0.0154

$\overline{CV}_{A+\overline{DE}}$ 0.0167

Data Sheet: Cyclohexanol S54

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.902	0.916	9.35	97.9	94	104.2
	0.938	0.952	9.50	100.2	94	106.6
	0.822	0.834	9.20	90.7	94	96.5
	0.905	0.918	9.50	96.7	94	102.8
	0.837	0.849	8.85	95.9	94	102.0
	0.882	0.895	9.30	96.2	94	102.3
			n = 6			
			mean	96.3		102.4
			std dev	3.2		
			CV_2	0.0328		
1.0	1.763	1.789	8.95	199.9	202	99.0
	1.916	1.943	10.15	191.5	202	94.8
	1.845	1.872	9.95	188.2	202	93.2
	1.561	1.584	9.05	175.0	202	86.6
	1.744	1.770	9.30	190.3	202	94.2
	1.578	1.601	9.05	176.9	202	87.6
			n = 6			
			mean	186.9		92.5
			std dev	9.4		
			CV_2	0.0504		
	3.237	3.284	9.85	333.4	378	88.2
	3.629	3.682	8.85	416.0	378	110.1
	3.371	3.420	9.25	369.7	378	97.8
	3.420	3.469	9.20	377.1	378	99.8
	3.826	3.881	9.05	428.9	378	113.5
	3.654	3.707	9.65	384.1	378	101.6
			n = 6			
			mean	384.9		101.8
			std dev	34.2		
			CV_2	0.0889	$\overline{CV}_2$	0.0620

BACKUP DATA REPORT

Substance:	Diacetone Alcohol, No. S55
OSHA Standard:	50 ppm (240 mg/cu m)
Chemical used for validation:	4-Hydroxy-4-methyl-2-pentanone, White Label Eastman Organic Chemical

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 600 mg/ml solution of diacetone alcohol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 5% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-pentadecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 56 percent. Addition of 5 percent of 2-propanol raised the desorption efficiency to 91.5 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.4 liters per minute, and the rate of diacetone alcohol injection was 0.7074 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 502 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration had reached only 2 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 24.1 mg of diacetone alcohol and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

Bartlett's test (Reference 3) for homogeneity of variance gave a chi squared value of 11.773, indicating that the hypothesis of equal variance can be rejected at a probability less than 0.01. However, the data for diacetone alcohol show acceptable precision. Therefore pooling should not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference 4.

$$\overline{CV}_1 = 0.0542 \qquad \overline{CV}_2 = 0.0883 \qquad \overline{CV}_T = 0.1038$$

The average recovery of the generated samples over all levels was:

91.8%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Backup Data Report for Propylene Oxide, No. S75, ibid.
4. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Diacetone Alcohol S55

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.120	0.836	0.746	2.330	1.951	0.837	4.660	3.543	0.760
1.120	0.813	0.726	2.330	1.578	0.677	4.660	3.763	0.808
1.120	0.836	0.746	2.330	1.153	(0.495)*	4.660	3.703	0.795
1.120	0.912	0.814	2.330	1.815	0.779	4.660	3.711	0.796
1.120	0.820	0.732	2.330	1.926	0.827	4.660	3.752	0.805
1.120	0.820	0.732	2.330	1.926	0.827	4.660	3.691	0.792
n =		6			5			6
mean		0.749			0.789			0.793
std dev		0.0328			0.0668			0.0170
CV_1		0.0437			0.0846			0.0214

CV_1 0.0542

$\overline{CV_{A+DE}}$ 0.0585

*Value deleted as outlier.

Data Sheet: Diacetone Alcohol S55

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.931	1.240	9.35	132.6	142	93.4
	0.891	1.192	9.50	125.5	142	88.4
	0.830	1.120	9.20	121.8	142	85.8
	0.903	1.206	8.85	136.3	142	96.0
	0.963	1.278	9.30	137.4	142	96.8
	0.988	1.307	9.50	137.6	142	96.9
			n = 6			
			mean	131.9		92.9
			std dev	6.7		
			CV_2	0.0510		
1S	1.777	2.254	8.95	251.8	290	86.8
	2.047	2.583	10.15	254.5	290	87.8
	2.117	2.669	9.95	268.2	290	92.5
	1.772	2.247	9.05	248.3	290	85.6
	1.879	2.378	9.30	255.7	290	88.2
	1.820	2.306	9.05	254.8	290	87.9
			n = 6			
			mean	255.6		88.1
			std dev	6.8		
			CV_2	0.0264		
2S	3.215	4.039	9.85	410.1	510	80.4
	3.545	4.460	8.85	504.0	510	98.8
	3.632	4.572	9.22	494.2	510	96.9
	3.887	4.900	9.00	541.5	510	106.2
	4.214	5.325	9.65	551.8	510	108.2
	3.156	3.965	10.25	386.8	510	75.8
			n = 6			
			mean	481.4		94.4
			std dev	68.2		
			CV_2	0.1417	$\overline{CV}_2$	0.0883

BACKUP DATA REPORT

Substance: Ethyl Alcohol, No. S56

OSHA Standard: 1000 ppm (1885 mg/cu m)

Chemical used for validation: Ethanol, absolute

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat ethyl alcohol injected with a 10-µl microliter syringe. The amount of solution added was 1.2, 2.4, and 4.8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 1 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-butanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-undecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 72.6 percent. Addition of 1 percent of 2-butanol raised the desorption efficiency to 90.2 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of this report. The total gas flow rate of the first stage was 23.4 liters per minute, and the rate of ethyl alcohol injection was 5.075 g/hr. Sampling time was 5 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 3273 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 8 minutes. Thus the capacity of this lot of charcoal is 5.2 mg of ethyl alcohol and at the recommended sampling rate, the breakthrough volume is 1.6 liters. Accordingly the sampling time was reduced to 5 minutes (sampling volume 1 liter).

Precision and Accuracy

Bartlett's test (Reference 2) for homogeneity of variance gave a chi squared value of 13.435, indicating that the hypothesis of equal variance can be rejected at a probability less than 0.01. However, the data for ethyl alcohol show excellent precision. Therefore pooling should not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.0269 \qquad \overline{CV}_2 = 0.0415 \qquad \overline{CV}_T = 0.0650$$

The average recovery of the generated samples over all levels was:

103.6%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Propylene Oxide, No. S75, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Ethyl Alcohol S56

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.950	0.715	0.752	1.900	1.543	0.812	3.800	3.231	0.850
0.950	0.736	0.775	1.900	1.475	0.776	3.800	3.187	0.839
0.950	0.741	0.780	1.900	1.553	0.818	3.800	3.133	0.824
0.950	0.696	0.733	1.900	1.477	0.777	3.800	3.226	0.849
0.950	0.265	(0.279)*	1.900	1.461	0.769	3.800	3.200	0.842
0.950	0.674	0.710	1.900	1.488	0.783	3.800	3.210	0.845
n =		5			6			6
mean		0.750			0.789			0.842
std dev		0.0292			0.0203			0.0094
CV_1		0.0390			0.0258			0.0111

$\overline{CV_1}$ 0.0269

$\overline{CV_{A+\overline{DE}}}$ 0.0290

*Value deleted as outlier.

Data Sheet: Ethyl Alcohol S56

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.668	0.895	0.935	957	902	106.1
	0.658	0.883	0.950	930	902	103.1
	0.670	0.897	0.920	975	902	108.1
	0.674	0.903	0.950	951	902	105.4
	0.631	0.849	0.885	960	902	106.4
	0.674	0.902	0.930	970	902	107.6
			n = 6			
			mean	957.2		106.1
			std dev	16.14		
			CV_2	0.0169		
1S	1.261	1.617	0.895	1807	1839	98.2
	1.416	1.802	1.015	1775	1839	96.5
	1.421	1.807	0.995	1817	1839	98.8
	1.278	1.637	0.905	1809	1839	98.4
	1.300	1.694	0.930	1822	1839	99.1
	1.239	1.590	0.905	1757	1839	95.5
			n = 6			
			mean	1897.6		97.8
			std dev	25.8		
			CV_2	0.0143		
2S	2.496	3.074	0.985	3120	3298	94.6
	2.654	3.242	0.885	3663	3298	111.1
	2.680	3.288	0.925	3554	3298	107.8
	2.675	3.283	0.920	3568	3298	108.2
	2.718	3.468	0.905	3832	3298	116.2
	2.587	3.303	0.955	3423	3298	103.8
			n = 6			
			mean	3426.8		106.9
			std dev	231.0		
			CV_2	0.0684	$\overline{CV}_2$	0.0415

BACKUP DATA REPORT

Substance:	Isoamyl Alcohol, No. S58
OSHA Standard:	100 ppm (360 mg/cu m)
Chemical used for validation:	3-Methyl-1-butanol, 99% Chemical Samples Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat isoamyl alcohol injected with a 10-µl microliter syringe. The amount added was 2.2, 4.5, and 9.0 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 5% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-tetradecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels were not in the proper order and differed by less than one standard deviation, therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 74.3 percent. Addition of 5 percent of 2-propanol raised the desorption efficiency to 98 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of isoamyl alcohol injection was 1.23 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 595 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 2 hours, 50 minutes. Thus the capacity of this lot of charcoal is 20 mg of isoamyl alcohol and at the recommended sampling rate, the breakthrough volume is 34 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$\overline{CV_1} = 0.0195 \qquad \overline{CV_2} = 0.0577 \qquad \overline{CV_T} = 0.0768$

The average recovery of the generated samples over all levels was:

107.6%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Isoamyl Alcohol S58

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.800	1.842	1.024	3.600	3.519	0.978	7.200	7.034	0.977
1.800	1.874	1.041	3.600	3.501	0.973	7.200	7.018	0.975
1.800	1.766	0.981	3.600	3.522	0.978	7.200	7.134	0.991
1.800	1.858	1.032	3.600	3.496	0.971	7.200	6.907	0.959
1.800	1.818	1.010	3.600	3.532	0.981	7.200	7.066	0.981
1.800	1.727	0.960	3.600	3.552	0.987	7.200	6.974	0.969
n =		6			6			6
mean		1.008			0.978			0.975
std dev		0.0316			0.0057			0.0108
CV_1		0.0314			0.0058			0.0111

$\overline{CV_1}$ 0.0195

$\overline{CV_{A+\overline{DE}}}$ 0.0210

220<

Data Sheet: Isoamyl Alcohol S58

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.853	1.842	9.35	197.0	194	101.6
	1.798	1.783	9.50	187.7	194	96.8
	2.008	2.007	9.20	218.1	194	112.4
	2.059	2.061	9.50	217.0	194	111.8
	1.823	1.810	8.85	204.6	194	105.4
	1.925	1.918	9.30	206.3	194	106.3
			n = 6			
			mean	205.1		105.7
			std dev	11.7		
			CV_2	0.0569		
1S	3.458	3.537	8.95	395.2	385	102.6
	3.873	3.970	10.15	391.1	385	101.6
	4.026	4.129	9.95	414.9	385	107.8
	3.662	3.750	9.05	414.3	385	107.6
	3.642	3.728	9.30	400.9	385	104.1
	3.445	3.523	9.05	389.3	385	101.1
			n = 6			
			mean	400.9		104.1
			std dev	11.3		
			CV_2	0.0283		
2S	6.310	6.477	9.85	657.6	678	97.0
	6.912	7.086	8.85	800.7	678	118.1
	7.004	7.180	9.25	776.2	678	114.5
	6.926	7.101	9.20	771.8	678	113.8
	7.354	7.532	9.00	832.2	678	122.7
	7.197	7.373	9.65	764.1	678	112.7
			n = 6			
			mean	767.1		113.1
			std dev	59.1		
			CV_2	0.0771	$\overline{CV}_2$	0.0577

BACKUP DATA REPORT

Substance:	Methyl Alcohol, No. S59
OSHA Standard:	200 ppm (260 mg/cu m)
Chemical used for validation:	Methanol, Reagent Grade J. T. Baker Chemicals Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of silica gel were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat methyl alcohol injected with a 10-µl microliter syringe. The amount added was 0.8, 1.65, and 3.3 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 5 liter air sample at the respective level. The eluting solvent was water. The silica gel tubes were supplied by SKC, Pittsburgh, Pennsylvania, Catalog Number 226-10. Gas chromatographic analysis were performed with an automatic sampler using absolute area calibration. Details of the analytical procedures are given in the Analytical Procedure section of Reference 1.

Modifications

The method was patterned after P&CAM 127, except that silica gel was used as the absorbent. It is possible to get satisfactory desportion of methyl alcohol from charcoal (Lot 105, SKC) by using carbon disulfide containing isobutyl alcohol. However, breakthrough (determined as described in the breakthrough section) for charcoal occurred in less than 2 minutes. Therefore, charcoal could not be used. Silica gel was found to be a satisfactory absorbent. Water was used as eluent, which satisfactorily desorbed the methanol.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.4 liters per minute, and the rate of methyl alcohol injection was 0.77 g/hr. Sampling time was 25 minutes with a nominal flow rate of 200 ml/min for each silica gel tube.

Breakthrough

In order to test the capacity of the silica gel tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 541 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube

reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing silica gel only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 52 minutes. Thus the capacity of the silica gel is 5.6 mg of methyl alcohol and at the recommended sampling rate, the breakthrough volume is 10.4 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$CV_1 = 0.1050 \qquad CV_2 = 0.0346 \qquad CV_T = 0.0633$$

The average recovery of the generated samples over all levels was:

94.2%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Methyl Alcohol S59

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.650	0.501	0.771	1.300	1.134	0.872	2.600	2.691	1.035
0.650	0.590	0.908	1.300	1.174	0.903	2.600	2.559	0.984
0.650	0.495	0.762	1.300	1.169	0.899	2.600	1.980	0.762
0.650	0.426	0.656	1.300	1.236	0.951	2.600	2.325	0.894
0.650	0.622	0.957	1.300	1.226	0.943	2.600	2.507	0.964
0.650	0.631	0.971	1.300	1.204	0.926	2.600	2.466	0.949
n = 6		6			6			6
mean		0.838			0.916			0.931
std dev		0.1267			0.0298			0.0950
CV_1		0.1513			0.0325			0.1020

CV_1 0.1070

$\overline{CV}_{A+\overline{DE}}$ 0.1156

Data Sheet: Methyl Alcohol S59

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.564	0.655	4.675	140.1	153	91.6
	0.574	0.668	4.750	140.6	153	91.9
	0.544	0.631	4.600	137.3	153	89.7
	0.569	0.661	4.750	139.2	153	91.0
	0.546	0.633	4.425	143.1	153	93.6
	0.582	0.677	4.650	145.6	153	95.2
			n = 6			
			mean	141.0		92.1
			std dev	3.0		
			CV_2	0.0211		
1S	1.114	1.288	4.475	287.7	311	92.5
	1.246	1.431	5.075	282.0	311	90.7
	1.150	1.327	4.975	266.8	311	85.8
	1.124	1.298	4.525	286.9	311	92.3
	1.203	1.385	4.650	297.9	311	95.8
	1.088	1.259	4.525	278.3	311	89.5
			n = 6			
			mean	283.3		91.1
			std dev	10.4		
			CV_2	0.0368		
2S	2.680	2.763	4.925	561.1	548	102.4
	2.308	2.457	4.425	555.2	548	101.3
	2.475	2.598	4.625	561.7	548	102.5
	2.421	2.553	4.600	554.9	548	101.3
	2.272	2.425	4.525	536.0	548	97.8
	2.269	2.423	4.825	502.2	548	91.6
			n = 6			
			mean	545.2		99.5
			std dev	23.0		
			CV_2	0.0423	$\overline{CV}_2$	0.0346

BACKUP DATA REPORT

Substance:	Methyl Isobutyl Carbinol, No. S60
OSHA Standard:	25 ppm (105 mg/cu m)
Chemical used for validation:	4-Methyl-2-pentanol, 99% Chemical Samples Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 250 mg/ml solution of methyl isobutyl carbinol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 5% ?-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-tetradecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels were not in the proper order and differed by less than one standard deviation, therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 67.9 percent. Addition of 5 percent of 2-propanol raised the desorption efficiency to 96 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of methyl isobutyl carbinol injection was 0.276 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 237 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration was less than 1 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 11.3 mg of methyl isobutyl carbinol and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV_1} = 0.0350 \qquad \overline{CV_2} = 0.0622 \qquad \overline{CV_T} = 0.0800$$

The average recovery of the generated samples over all levels was:

101.8%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Methyl Isobutyl Carbinol S60

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.500	0.507	1.015	1.000	0.995	0.995	2.000	1.988	0.994
0.500	0.513	1.026	1.000	0.988	0.988	2.000	1.966	0.983
0.500	0.510	1.019	1.000	0.978	0.978	2.000	1.945	0.972
0.500	0.441	0.881	1.000	0.985	0.985	2.000	1.947	0.974
0.500	0.515	1.031	1.000	0.998	0.998	2.000	1.917	0.958
0.500	0.506	1.012	1.000	0.993	0.993	2.000	1.892	0.946
n =		6			6			6
mean		0.997			0.989			0.971
std dev		0.0573			0.0075			0.0172
CV_1		0.0574			0.0075			0.0177

CV_1 0.0350

$\overline{CV}_{A+\overline{DE}}$ 0.0378

Data Sheet: Methyl Isobutyl Cardinol S60

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.431	0.437	9.35	46.8	43	108.8
	0.439	0.445	9.50	46.8	43	108.9
	0.447	0.454	9.20	49.3	43	114.6
	0.450	0.456	9.50	48.1	43	111.7
	0.374	0.380	8.85	42.9	43	99.7
	0.458	0.464	9.30	49.9	43	116.2
			n = 6			
			mean	47.3		110.0
			std dev	2.5		
			CV_2	0.0530		
1S	0.846	0.858	8.95	95.9	100	95.9
	0.939	0.953	10.15	93.9	100	93.9
	0.911	0.924	9.95	92.8	100	92.8
	0.741	0.752	9.05	83.1	100	83.1
	0.871	0.884	9.30	95.1	100	95.1
	0.841	0.853	9.05	94.3	100	94.3
			n = 6			
			mean	92.5		92.5
			std dev	4.7		
			CV_2	0.0512		
2S	1.568	1.591	9.85	161.6	177	91.3
	1.673	1.697	8.85	191.8	177	108.4
	1.708	1.733	9.25	187.3	177	105.8
	1.610	1.633	9.20	177.5	177	100.3
	1.794	1.820	9.05	201.1	177	113.6
	1.639	1.663	9.65	172.3	177	97.3
			n = 6			
			mean	181.9		102.8
			std dev	14.3		
			CV_2	0.0786	$\overline{CV}_2$	0.0622

BACKUP DATA REPORT

Substance:	Propyl Alcohol S62
OSHA Standard:	200 ppm (490 mg/cu m)
Chemical used for validation:	1-Propanol, Reagent Grade J. T. Baker Chemical Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 625 mg/ml solution of propyl alcohol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-undecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 69 percent. Addition of 1 percent of 2-propanol raised the desorption efficiency to 86.5 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of propyl alcohol injection was 1.43 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 946 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 1 hour, 35 minutes. Thus the capacity of this lot of charcoal is 18 mg of propyl alcohol and at the recommended sampling rate, the breakthrough volume is 19 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$\overline{CV_1} = 0.0162 \qquad \overline{CV_2} = 0.0555 \qquad \overline{CV_T} = 0.0750$

The average recovery of the generated samples over all levels was:

103.5%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Propyl Alcohol S62

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
2.50	2.15	0.858	5.00	4.50	0.899	10.00	9.38	0.938
2.50	2.15	0.858	5.00	4.45	0.891	10.00	9.01	0.901
2.50	2.23	0.893	5.00	4.45	0.891	10.00	9.20	0.920
2.50	2.15	0.861	5.00	4.46	0.892	10.00	9.27	0.927
2.50	2.11	0.845	5.00	4.42	0.883	10.00	8.90	0.899
2.50	2.11	0.845	5.00	4.43	0.886	10.00	9.00	0.900
n =		6			6			6
mean		0.860			0.890			0.914
std dev		0.0176			0.0054			0.0168
CV_1		0.0205			0.0061			0.0183

$\overline{CV}_1$ 0.0162

$\overline{CV}_{A+\overline{DE}}$ 0.0176

Data Sheet: Propyl Alcohol S62

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.873	2.187	9.35	233.9	224	104.4
	1.921	2.240	9.50	235.8	224	105.2
	1.787	2.091	9.20	227.3	224	101.5
	1.897	2.213	9.50	232.9	224	104.0
	1.768	2.070	8.85	233.9	224	104.4
	1.954	2.276	9.30	244.8	224	109.3
			n = 6			
			mean	234.7		104.8
			std dev	5.7		
			CV_2	0.0242		
1S	3.667	4.161	8.95	464.9	458	101.5
	4.004	4.527	10.15	446.0	458	97.4
	4.009	4.533	9.95	455.6	458	99.5
	3.504	3.982	9.05	440.0	458	96.1
	4.000	4.523	9.30	486.3	458	106.2
	3.554	4.036	9.05	446.0	458	97.4
			n = 6			
			mean	456.5		99.7
			std dev	17.1		
			CV_2	0.0374		
2S	7.241	7.999	9.85	812.1	833	97.5
	7.737	8.522	8.85	962.9	833	115.6
	7.252	8.011	9.25	866.1	833	104.0
	6.640	7.363	9.20	800.3	833	96.1
	8.074	8.876	9.00	980.8	833	117.7
	7.626	8.406	9.65	871.0	833	104.6
			n = 6			
			mean	882.2		105.9
			std dev	75.2		
			CV_2	0.0852	$\overline{CV}_2$	0.0555

BACKUP DATA REPORT

Substance:	tert-Butyl Alcohol, No. S63
OSHA Standard:	100 ppm (305 mg/cu m)
Chemical used for validation:	tert-Butyl Alcohol, Reagent J. T. Baker Chemicals Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 750 mg/ml solution of tert-butyl alcohol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-butanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-undecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 87.5 percent. Addition of 1 percent of 2-butanol raised the desorption efficiency to 92.1 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of tert-butyl alcohol injection was 0.941 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 580 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 1 hour, 25 minutes. Thus the capacity of this lot of charcoal is 9.9 mg of tert-butyl alcohol and at the recommended sampling rate, the breakthrough volume is 17 liters. This meets the above requirement.

Precision and Accuracy

Bartlett's test (Reference 3) for homogeneity of variance gave a chi squared value of 13.582, indicating that the hypothesis of equal variance can be rejected at a probability less than 0.01. However, the data for tert-butyl alcohol show excellent precision. Therefore pooling should not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference 4.

$$\overline{CV}_1 = 0.0183 \qquad \overline{CV}_2 = 0.0554 \qquad \overline{CV}_T = 0.0750$$

The average recovery of the generated samples over all levels was:

100.3%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Backup Data Report for Propylene Oxide, No. S75, ibid.
4. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: tert-Butyl Alcohol S63

Analysis

Level	0.5S		1S			2S		
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.500	1.312	0.875	3.000	2.772	0.924	6.000	5.591	0.932
1.500	1.325	0.884	3.000	2.706	0.902	6.000	5.465	0.911
1.500	1.331	0.887	3.000	2.761	0.920	6.000	5.497	0.916
1.500	1.398	0.932	3.000	2.667	0.889	6.000	5.468	0.911
1.500	1.330	0.887	3.000	2.725	0.908	6.000	5.615	0.936
1.500	1.382	0.921	3.000	2.757	0.919	6.000	5.537	0.923
n =		6			6			6
mean		0.898			0.910			0.922
std dev		0.0231			0.0133			0.0106
CV_1		0.0258			0.0146			0.0115

$\overline{CV_1}$ 0.0183

$\overline{CV_{A+\overline{DE}}}$ 0.0198

Data Sheet: tert-Butyl Alcohol S63

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.434	1.596	9.35	170.7	166	102.8
	1.455	1.618	9.50	170.3	166	102.6
	1.377	1.533	9.20	166.7	166	100.4
	1.436	1.598	9.50	168.2	166	101.3
	1.311	1.462	8.85	165.2	166	99.5
	1.390	1.548	9.30	166.4	166	100.3
			n = 6			
			mean	167.9		101.2
			std dev	2.2		
			CV_2	0.0132		
1S	2.666	2.932	8.95	327.6	339	96.6
	2.971	3.261	10.15	321.3	339	94.8
	2.893	3.176	9.95	319.2	339	94.2
	2.598	2.858	9.05	315.8	339	93.2
	2.732	3.002	9.30	322.8	339	95.2
	2.560	2.817	9.05	311.2	339	91.8
			n = 6			
			mean	319.7		94.3
			std dev	5.7		
			CV_2	0.0178		
2S	5.168	5.614	9.85	570.0	602	94.7
	5.488	5.954	8.85	672.7	602	111.7
	5.334	5.790	9.25	626.0	602	104.0
	5.268	5.721	9.20	621.8	602	103.3
	5.786	6.271	9.05	692.9	602	115.1
	5.591	6.063	9.55	628.3	602	104.4
			n = 6			
			mean	635.3		105.5
			std dev	43.1		
			CV_2	0.0679	$\overline{CV}_2$	0.0412

BACKUP DATA REPORT

Substance:	Isobutyl Alcohol, No. S64
OSHA Standard:	100 ppm (305 mg/cu m)
Chemical used for validation:	2-Methyl-1-butanol, 99% Chemical Samples Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 750 mg/ml solution isobutyl alcohol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-dodecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 81.6 percent. Addition of 1 percent of 2-propanol raised the desorption efficiency to 92.8 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of isobutyl alcohol injection was 0.960 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 669 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred at 2 hours, 35 minutes. Thus the capacity of this lot of charcoal is 21 mg of isobutyl alcohol and at the recommended sampling rate, the breakthrough volume is 31 liters. This meets the above requirement.

Precision and Accuracy

Bartlett's test (Reference 3) for homogeneity of variance gave a chi squared value of 11.428, indicating that the hypothesis of equal variance can be rejected at a probability less than 0.01. However, the data for isobutyl alcohol show excellent precision. Therefore pooling should not introduce significant error. For this reason $\overline{CV_T}$ is calculated on all the data.

The statistical procedures used are described in Reference 4.

$$\overline{CV_1} = 0.0231 \qquad \overline{CV_2} = 0.0518 \qquad \overline{CV_T} = 0.0726$$

The average recovery of the generated samples over all levels was:

100.0%

References

1. Backup data Report for Camphor, No. S10.
2. Backup Data Report for Ethyl Alcohol, No. S56.
3. Backup Data Report for Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.
4. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Isobutyl Alcohol S64

Analysis

Level	0.5S		1S			2S		
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.500	1.250	0.834	3.000	2.583	0.861	6.000	5.339	0.890
1.500	1.245	0.830	3.000	2.554	0.851	6.000	5.260	0.877
1.500	1.142	0.761	3.000	2.545	0.848	6.000	5.293	0.882
1.500	1.205	0.804	3.000	2.560	0.853	6.000	5.302	0.884
1.500	1.269	0.846	3.000	2.535	0.845	6.000	5.431	0.905
1.500	1.240	0.827	3.000	2.512	0.837	6.000	5.315	0.886
n =		6			6			6
mean		0.817			0.849			0.887
std dev		0.0305			0.0079			0.0098
CV_1		0.0373			0.0093			0.0110

$\overline{CV_1}$ 0.0231

$\overline{CV_{A+DE}}$ 0.0250

Data Sheet: Isobutyl Alcohol S64

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.367	1.664	9.35	178.0	179	99.4
	1.359	1.655	9.50	174.2	179	97.3
	1.364	1.660	9.20	180.4	179	100.8
	1.392	1.692	9.50	178.1	179	99.5
	1.376	1.673	8.85	189.1	179	105.6
	1.534	1.855	9.30	199.5	179	111.4
			n = 6			
			mean	183.2		102.3
			std dev	9.4		
			CV_2	0.0514		
1S	2.520	2.969	8.95	331.7	360	92.1
	2.874	3.363	10.15	331.3	360	92.0
	1.680	2.021	9.95	(203.2)*	360	(56.4)*
	2.582	3.039	9.05	335.8	360	93.3
	2.689	3.158	9.30	339.6	360	94.3
	2.582	3.039	9.05	335.8	360	93.3
			n = 5			
			mean	334.8		93.0
			std dev	3.42		
			CV_2	0.0102		
2S	5.060	5.723	9.85	581.0	621	93.6
	5.519	6.202	8.85	700.8	621	112.9
	5.207	5.877	9.25	635.4	621	102.3
	5.237	5.908	9.20	642.2	621	103.4
	5.653	6.342	9.00	700.7	621	112.8
	5.483	6.165	9.65	638.9	621	102.9
			n = 6			
			mean	649.8		104.6
			std dev	45.4		
			CV_2	0.0699	$\overline{CV}_2$	0.0518

*Value deleted as outlier.

BACKUP DATA REPORT

Substance:	Isopropyl Alcohol, No. S65
OSHA Standard:	400 ppm (985 mg/cu m)
Chemical used for validation:	2-Propanol, distilled in glass Burdick and Jackson

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat isopropyl alcohol injected with a 10-µl microliter syringe. The amount added was 6.3, 12.5, and 25 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 2.5 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-butanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-undecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels were not in the proper order and differed by less than one standard deviation, therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 86.4 percent. Addition of 1 percent of 2-butanol raised the desorption efficiency to 95.8 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.4 liters per minute, and the rate of isopropyl alcohol injection was 3.069 g/hr. Sampling time was 12.5 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 1890 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 30 minutes. Thus the capacity of this lot of charcoal is 11.3 mg of isopropyl alcohol and at the recommended sampling rate, the breakthrough volume is 6 liters. Accordingly, the sampling time was reduced to 12.5 minutes (sampling volume 2.5 liters).

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV_1} = 0.0330 \qquad \overline{CV_2} = 0.0383 \qquad \overline{CV_T} = 0.0644$$

The average recovery of the generated samples over all levels was:

96.7%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Isopropyl Alcohol S65

Analysis

Level	0.5S		1S			2S		
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.225	1.172	0.956	2.450	2.316	0.945	4.900	4.597	0.938
1.225	1.087	0.887	2.450	2.306	0.941	4.900	4.587	0.936
1.225	1.203	0.982	2.450	2.347	0.958	4.900	4.536	0.926
1.225	1.207	0.986	2.450	2.139	0.873	4.900	4.539	0.926
1.225	1.176	0.960	2.450	2.357	0.962	4.900	4.437	0.906
1.225	1.113	0.908	2.450	2.243	0.915	4.900	4.498	0.918
n =		6			6			6
mean		0.947			0.932			0.925
std dev		0.0401			0.0335			0.0120
CV_1		0.0424			0.0359			0.0130

CV_1 0.0330

$\overline{CV_{A+DE}}$ 0.0356

Data Sheet: Isopropyl Alcohol S65

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.046	1.118	2.34	478	506	94.5
	1.046	1.118	2.37	471	506	93.0
	1.077	1.151	2.30	500	506	98.9
	1.066	1.139	2.37	480	506	94.8
	1.029	1.100	2.21	497	506	98.2
	1.103	1.179	2.32	507	506	100.3
			n = 6			
			mean	488.9		96.6
			std dev	14.6		
			CV_2	0.0299		
1S	1.988	2.125	2.24	950	1014	93.7
	2.188	2.339	2.54	922	1014	90.9
	2.224	2.377	2.49	956	1014	94.3
	1.945	2.079	2.26	919	1014	90.6
	2.044	2.185	2.32	940	1014	92.7
	2.034	2.174	2.26	961	1014	94.8
			n = 6			
			mean	941.2		92.8
			std dev	17.6		
			CV_2	0.0187		
2S	4.086	4.368	2.46	1774	1891	93.8
	4.108	4.391	2.21	1985	1891	105.0
	4.040	4.318	2.31	1867	1891	98.8
	3.909	4.179	2.30	1817	1891	96.1
	4.361	4.662	2.25	2061	1891	109.0
	4.318	4.616	2.39	1913	1891	101.2
			n = 6			
			mean	1902.8		100.6
			std dev	106.7		
			CV_2	0.0561	$\overline{CV}_2$	0.0383

BACKUP DATA REPORT

Substance:	Butyl Alcohol, No. S66
OSHA Standard:	100 ppm (305 mg/cu m)
Chemical used for validation:	1-Butanol, 99% Chemical Samples Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 750 mg/ml solution of butyl alcohol in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10 liter air sample at the respective level. The eluting solvent was carbon disulfide containing 1% 2-propanol. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-dodecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. An internal standard was added for improved accuracy. Carbon disulfide as eluent gave a desorption efficiency of 77.3 percent. Addition of 1 percent of 2-propanol raised the desorption efficiency to 84.4 percent.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 24.2 liters per minute, and the rate of butyl alcohol injection was 0.934 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 600 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion was used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred at 2 hours, 55 minutes. Thus the capacity of this lot of charcoal is 21 mg of butyl alcohol and at the recommended sampling rate, the breakthrough volume is 35 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$\overline{CV_1} = 0.0208$ $\overline{CV_2} = 0.0412$ $\overline{CV_T} = 0.0653$

The average recovery of the generated samples over all levels was:

100.0%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Butyl Alcohol S66

Analysis

Level	0.5S			1S			2S		
	mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
	1.500	1.391	0.928	3.000	2.617	0.872	6.000	5.430	0.905
	1.500	1.338	0.892	3.000	2.696	0.899	6.000	5.405	0.901
	1.500	1.302	0.868	3.000	2.672	0.891	6.000	5.346	0.891
	1.500	1.284	0.856	3.000	2.593	0.864	6.000	5.436	0.906
	1.500	1.312	0.875	3.000	2.636	0.879	6.000	5.388	0.898
	1.500	1.276	0.851	3.000	2.617	0.872	6.000	5.449	0.908
n =			6			6			6
mean			0.878			0.880			0.902
std dev			0.0283			0.0128			0.0063
CV_1			0.0322			0.0146			0.0070

$\overline{CV_1}$ 0.0208

$\overline{CV_{A+DE}}$ 0.0225

Data Sheet: Butyl Alcohol S66

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.455	1.659	9.35	177.5	170	104.4
	1.248	1.422	9.50	149.7	170	88.1
	1.426	1.627	9.20	176.8	170	104.0
	1.487	1.697	9.50	178.6	170	105.1
	1.370	1.563	8.85	176.6	170	103.9
	1.429	1.630	9.30	175.2	170	103.1
			n = 6			
			mean	172.4		101.4
			std dev	11.2		
			CV_2	0.0648		
1S	2.683	3.049	8.95	340.7	353	96.5
	2.807	3.186	10.15	313.9	353	88.9
	2.895	3.284	9.95	330.1	353	93.5
	2.703	3.071	9.05	339.3	353	96.1
	2.747	3.120	9.30	335.5	353	95.0
	2.598	2.954	9.05	326.4	353	92.5
			n = 6			
			mean	331.0		93.8
			std dev	10.0		
			CV_2	0.0301		
2S	5.150	5.726	9.85	581.4	610	95.3
	5.477	6.070	8.85	685.9	610	112.4
	5.296	5.881	9.25	635.8	610	104.2
	5.224	5.805	9.20	630.9	610	103.4
	5.620	6.220	9.00	687.3	610	112.7
	5.372	5.960	9.65	617.6	610	101.3
			n = 6			
			mean	640.0		104.9
			std dev	40.9		
			CV_2	0.0640	$\overline{CV}_2$	0.0554

Backup Data Report

Substance:	Chlorinated Camphene, No. S67
OSHA Standard:	0.5 mg/cu m
Chemical used for validation:	Toxaphene, X-16189-13 Hercules Incorporated

Procedure

The general procedure used is described in NIOSH Method No. S67, which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for gas chromatographic analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 15-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot (2, 4, and 8 microliters) of a 1.74 mg/ml solution of the chlorinated camphene in petroleum ether* was added to 37-mm type AA Millipore filters. The chlorinated camphene was extracted from the filter with petroleum ether and analyzed in a Varian 1800 Gas Chromatograph with a nickel-63 electron capture detector. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S67.

Test atmospheres of chlorinated camphene at concentrations at 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on the Millipore filters in open-faced polystyrene filter cassettes. The results of analysis of these samples are given in the Sampling and Analysis table. The estimated average size of the particles was less than 1 micron diameter. The collection efficiency at 2X the OSHA standard was measured as described under Discussion for both particles and vapors which might have passed through the first filter. The collection efficiency for particles was considered to be 1.00 ± 0.01; no vapors were detected in a midget impinger containing ethylene glycol that followed several of the filters.

Modification

The method used for Sampling and Analysis was a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for gas chromatographic analysis of organic samples.

*Mallinckrodt Nanograde®, boiling range 30° to 60°C.

Generation

The test atmospheres were generated with an Environmental Research Corporation * model 7300 fluid atomization aerosol generator. This unit consists of a Collison type of fluid atomizer, an impactor which removes droplets with diameters greater than 5 microns, a dilution chamber where solvent evaporates from the aerosol droplets, and an ionizer to neutralize any electric charge on the particles.

The output of the aerosol generator was divided by a glass tee. The split ratio of the tee was controlled by the relative diameters of the two outlet branches of the tee. The portion of the air that entered the chamber through one arm of the tee was further diluted with air entering at a rate of 185 liters per minute (the flow was controlled by an orifice). The other arm of the tee was exhausted to a hood. The concentration of the generated atmosphere was dependent on the concentration of the solution in the atomizer, the flow rate of dilution air in the generator, and the fraction of the generator effluent which entered the chamber before the second dilution stage.

The stainless steel sampling chamber is in the shape of an inverted cone, approximately 2 ft high by 6 in diameter at the base. The base section contained the fittings necessary to connect six filter holders in a vertical position. These six sampling ports were connected through individual critical orifices to a metal bellows vacuum pump.

A 0.25% solution of chlorinated camphene in heptane (2.5 g chlorinated camphene made up to a 1-liter volume with heptane) was used in the atomizer. Samples of chlorinated camphene were generated and collected separately at each of three levels (0.5X, 1X, and 2X the OSHA standard). To monitor the concentration in the sampling chamber at each of the three levels, samples were collected, and analyses of the samples were made. When the desired concentration in the chamber was reached, six samples at each level were collected. Samples were collected for 15 minutes at a rate of approximately 1 liter per minute. Since collection efficiency was found to be 1.00 ± 0.01, the concentration in the generator and the "found" concentration were considered to be equal.

Discussion

It was necessary to use an indirect method of determining the concentration in the generator based on analysis of the collected samples and measurement of collection efficiency, because the concentration of chlorinated camphene particulates could not be measured directly. Collection efficiency was assessed in the following manner. The amount of particulates collected on each of two filters mounted back-to-back in a single filter cassette and the amount of vapor passing through

*Located in St. Paul, Minnesota

the filter and collected in a midget impinger were measured. The collection efficiency of the filter was considered to be 1.00, since no analyte was found either on the backup filter or in the backup midget impinger. It was demonstrated that as little as 1% of the chlorinated camphene in the sample could be found if it were present on the backup filter or impinger as follows.

Three cellulose filters were spiked with 0.696 microgram of chlorinated camphene * in petroleum ether, and analyzed as described in Section 8.4 of the sampling and analytical method. The data are summarized in Table 1.

Midget impingers containing ethylene glycol were used to measure the amount of chlorinated camphene vapors which might pass through the filter during sample collection. The extraction procedure for chlorinated camphene from ethylene glycol was adapted from P&CAM 158, except that petroleum ether was used as the extraction solvent. The analytical method recovery of this method was measured at 1.0 and 0.1 times the OSHA standard level. Three midget impingers containing 15 ml of ethylene glycol were spiked with 6.96 micrograms of chlorinated camphene in petroleum ether.*** Another set of three midget impingers containing ethylene glycol were spiked with 0.696 microgram of chlorinated camphene.*** Analytical method recovery (A.M.R.) for these spiked samples is summarized in Table 1.

$$\text{A.M.R.} = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

Table 1

ADDITIONAL RECOVERY DATA

CHLORINATED CAMPHENE

Collection Medium	Microgram taken	Microgram found	Recovery
Cellulose filters	0.696	0.703	1.010
	0.696	0.620	0.891
	0.696	0.606	0.871
Midget impingers containing ethylene glycol	6.96	6.55	0.941
	6.96	7.03	1.010
	6.96	7.03	1.010
	0.696	0.717	1.030
	0.696	0.717	1.030
	0.696	0.703	1.010

*Four microliters of a 0.174 mg/ml solution of chlorinated camphene in petroleum ether was used to spike filters and impingers with 0.696 microgram chlorinated camphene; four microliters of a 1.74 mg/ml solution of chlorinated camphene in petroleum ether was used to spike filters with 6.96 micrograms of chlorinated camphene.

The lower limit of detection of chlorinated camphene in a 10-ml extract was determined to be less than 0.14 microgram.*

Two separate collection efficiency experiments were carried out. In the first experiment, three 15-liter samples at 2X the OSHA standard (1.155 mg/cu m **) were collected.*** Each sample filter cassette was followed by a midget impinger containing 15 ml of ethylene glycol, to collect any vapors of chlorinated camphene. In the second experiment, four 30-liter samples at 1.265 mg/cu m ** were collected, using cassettes containing 2 filters back-to-back in the same cassette to measure the particulate collection efficiency of the filter. Each sample was analyzed as described above. In each case, the concentration of chlorinated camphene observed in the backup filter or impinger was below the limit of detection (0.14 microgram in a 10-ml extract). As a result of these experiments, the collection of the 0.8-micron pore size cellulose filter was considered to be 1.00 $\pm$ 0.01.

The stability of samples stored in a filter cassette was tested. Three filters were dosed at the 1X OSHA standard level. They were stored in cassettes at room temperature for one day and analyzed. The results reported in Table 2 are to be compared with the results in the Analysis Data Sheet for samples stored in glass beakers sealed with Parafilm. Using the data for the average mg found at the 1X level, an average loss of 17.7% was observed when samples were stored in the cassettes. Therefore, the method was modified to require that the exposed filters be transferred to screw cap glass bottles within one hour after sample collection.

Table 2

ANALYTICAL METHOD RECOVERY FOR SAMPLES OF CHLORINATED CAMPHENE STORED IN CASSETTE HOLDERS FOR ONE DAY

Amount dosed (Microgram)	Amount found when stored in cassette (Microgram)	Recovery
6.96	5.58	0.802
6.96	5.43	0.780
6.96	5.45	0.783
Average	5.49	0.788

*A 5-microliter aliquot of a 0.014 microgram/ml solution of chlorinated camphene in petroleum ether was injected into the gas chromatograph. A gas chromatogram showed the presence of chlorinated camphene, but the area under the curve could not be measured accurately with the electronic integrator.

**The concentration was calculated from the means of the concentrations determined by analyzing the front filter as described in the Sampling and Analytical Method and the preceding sections of this report.

***These samples were collected simultaneously with the samples used for sampling and analysis during the 2X OSHA standard generation experiment. Three of these six generated samples had midget impingers backups.

Precision and Accuracy

The statistical procedures used are described in Reference No. 1.

$\overline{CV}_1 = 0.022$ $\overline{CV}_2 = 0.056$ $\overline{CV}_T = 0.076$

Data Sheet: Chlorinated Camphene S67

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.00348	0.00314	0.902	0.00696	0.00685	0.984	0.01393	0.01320	0.948
0.00348	0.00315	0.905	0.00696	0.00638	0.914	0.01393	0.01391	0.998
0.00348	0.00329	0.945	0.00696	0.00657	0.944	0.01393	0.01364	0.979
0.00348	0.00311	0.894	0.00696	0.00665	0.955	0.01393	0.01376	0.988
0.00348	0.00319	0.917	0.00696	0.00671	0.964	0.01393	0.01354	0.972
0.00348	0.00319	0.917	0.00696	0.00688	0.989	0.01393	0.01350	0.969

n =	6	6	6
mean	0.913	0.958	0.976
std dev	0.018	0.028	0.017
CV_1	0.020	0.029	0.017

$\overline{CV}_1$ 0.022

$\overline{CV}_{A+\overline{DE}}$ 0.024

A curve of analytical method recovery vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis Table.

Data Sheet: Chlorinated Camphene S67

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m *
0.5S	0.00314	0.00345	13.67	0.2524
	0.00304	0.00334	14.72	0.2269
	0.00249	0.00282	14.23	0.1982
	0.00300	0.00331	14.64	0.2261
	0.00317	0.00347	14.83	0.2340
	0.00278	0.00309	14.52	0.2128
			n = 6	
			mean	0.2251
			std dev	0.0185
			CV_2	0.082
1S	0.00697	0.00726	13.67	0.531
	0.00784	0.00812	14.72	0.552
	0.00724	0.00753	14.23	0.529
	0.00703	0.00732	14.64	0.500
	0.00728	0.00756	14.83	0.510
	0.00706	0.00735	14.52	0.506
			n = 6	
			mean	0.521
			std dev	0.020
			CV_2	0.038
2S	0.01476	0.01512	13.52	1.118
	0.01678	0.01719	14.34	1.199
	0.01579	0.01618	13.52	1.197
	0.01505	0.01542	14.43	1.166
	0.01576	0.01615	14.15	1.141
	0.01524	0.01561	14.10	1.107
			n = 6	
			mean	1.155
			std dev	0.039
$\overline{CV}_2$	0.056		CV_2	0.034

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Dipropylene Glycol Methyl Ether, No. S69

OSHA Standard: 100 ppm (610 mg/cu m)

Chemical used for validation: Dipropylene Glycol Methyl Ether, Lot MM09174-153 Dow Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of dipropylene glycol methyl ether in air is described in NIOSH Method S69, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid dipropylene glycol methyl ether to represent 10 liter air samples. Samples of dipropylene glycol methyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of dipropylene glycol methyl ether in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.6 minutes). The "true" value for the concentration of dipropylene glycol methyl ether was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of dipropylene glycol methyl ether in air were generated by the procedure described in the Backup Data Report for 2-butoxy ethanol (Reference No. 1). The generator conditions used are given in the following table:

Generator Conditions
for
Dipropylene Glycol Methyl Ether

Nitrogen flow rate	3.49 liters/minute at 22°C
Dilution air flow rate	29.2 liters/minute at 22°C
Bath temperature	50°C

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 2). Samples were collected for 54.6 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 145 minutes when a concentration of 1219 mg/cu m was sampled at a rate of 0.185 liter per minute.

Discussion

A standard of dipropylene glycol methyl ether in carbon disulfide was prepared at the 1X OSHA standard level, and an aliquot of this standard was injected into the G.C. The resulting curve on the gas chromatogram had a major peak (85%) and a smaller shoulder (15%). Another standard of dipropylene glycol methyl ether was prepared in methylene chloride at 1X the OSHA standard level to test if an impurity in the carbon disulfide caused the second peak. The methylene chloride standard also gave a similar curve with the same shape and proportionality as the carbon disulfide standard. It was decided that the desorbing solvents used did not cause the shoulder, and carbon disulfide was used as the desorbing solvent for the method. It was also observed that shape and proportionality of peaks did not change in the desorption efficiency or generated samples; therefore, the larger peak was used to measure the amount of analyte, and the smaller peak was ignored.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.022$ $\overline{CV}_2 = 0.039$ $\overline{CV}_T = 0.064$

The average recovery at the OSHA standard level was 101.4%.

Data Sheet: Dipropylene Glycol Methyl Ether S69

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
2.954	1.710	0.579	6.00	4.87	0.812	12.01	10.81	0.900
2.954	1.805	0.611	6.00	4.77	0.795	12.01	10.34	0.861
2.954	1.820	0.616	6.00	4.72	0.787	12.01	10.89	0.907
2.954	1.838	0.622	6.00	4.66	0.777	12.01	10.78	0.898
2.954	1.730	0.586	6.00	4.67	0.778	12.01	10.71	0.892
2.954	1.798	0.609	6.00	4.80	0.800	12.01	10.68	0.889
n=		6			6			6
mean		0.604			0.792			0.891
std dev		0.017			0.014			0.016
CV_1		0.028			0.018			0.018

$\overline{CV}_1$ 0.022

$\overline{CV}_{A+\overline{DE}}$ 0.024

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Dipropylene Glycol Methyl Ether S69

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	2.102	3.27	10.16	322	314	
	2.004	3.17	10.11	314	314	
	1.996	3.16	10.11	312	314	
	2.189	3.35	10.11	331	314	
	2.193	3.36	10.27	327	314	
	2.050	3.22	9.95	324	314	
			n = 6			
			mean	322		102.4
			std dev	7		
			CV_2	0.022		
1S	4.54	5.78	8.96	645	621	
	4.32	5.56	8.42	660	621	
	4.86	6.11	9.56	639	621	
	3.97	5.19	9.07	572	621	
	4.92	6.18	9.24	669	621	
	4.41	5.65	9.56	591	621	
			n = 6			
			mean	629		101.4
			std dev	39		
			CV_2	0.062		
2S	11.36	12.68	10.11	1254	1197	
	11.34	12.66	10.11	1252	1197	
	11.49	12.81	10.16	1261	1197	
	10.94	12.25	9.95	1231	1197	
	11.47	12.79	10.11	1265	1197	
	11.06	12.37	10.27	1204	1197	
			n = 6			
			mean	1244		104.0
			std dev	23		
$\overline{CV}_2$	0.039		CV_2	0.018		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, 2-Butoxy Ethanol, No. S76, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Glycidol, No. S70
OSHA Standard:	150 mg/cu m
Chemical used for validation:	Glycidol, Lot 31 MC/B

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of glycidol in air is described in NIOSH Method S70, which has been adapted from P&CAM 127. Tetrahydrofuran rather than carbon disulfide was used to desorb the glycidol from the charcoal. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid glycidol to represent 50 liter air samples. Samples of glycidol in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of glycidol in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 53.5 minutes). The "true" value for the concentration of glycidol generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

Two major modifications to P&CAM 127 were made.

Tetrahydrofuran (THF) instead of carbon disulfide was used as the eluent in the method, because carbon disulfide gave poor recoveries. Results are summarized in the "Discussion" section of this report.

It was necessary to refrigerate the charcoal tubes after collection of glycidol because low recoveries were found if the samples were stored for more than a few hours at room temperature. Results for glycidol collected on charcoal with and without refrigeration during storage of the collected samples are given in the "Discussion" section of this report.

Generation

Samples of glycidol in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 1.93 liters per minute was bubbled through the glycidol in the generator flask, which was maintained at a temperature of 73°C. After passing through the condenser, which was water cooled at 20°C, the glycidol vapor was diluted to the 2X OSHA standard level with air added at a rate of 32.1 liters per minute. Two further dilutions were made to obtain concentrations at the 1X and 0.5X OSHA levels.

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 2). The three sampling chambers were monitored alternately during the time the samples were being collected. Samples were collected for 53.5 minutes at a rate of approximately 1 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 163 minutes when a concentration of 300 mg/cu m was sampled at a rate of 0.93 liter per minute.

Discussion

Several experiments were made to test the recovery of glycidol using different solvents. The experiment was done with glycidol samples that were unrefrigerated, because it was not known at this time that it was necessary to refrigerate the samples. The results are summarized in the table below.

Desorption Efficiency Trials

Solvent (0.5 ml each)	mg taken	mg found	D.E.
Carbon disulfide	7.84	1.74	0.2219
Carbon disulfide	7.84	1.77	0.2258
Methylene chloride	7.84	5.09	0.649
Methylene chloride with 5% methanol	7.84	5.61	0.715
Methylene chloride with 5% methanol	7.84	5.30	0.676
Methylene chloride with 5% methanol	14.97	9.6	0.646
Methylene chloride with 10% methanol	7.84	5.53	0.705
Tetrahydrofuran (THF)	7.84	6.12	0.780

It was noted that carbon disulfide gave the lowest recovery, and that THF gave the highest recovery. THF was selected for use in the procedure.

The desorption efficiency of glycidol, using SKC charcoal Lot 105 and THF as the solvent, was measured as specified in P&CAM 127. Spiked charcoal tubes were allowed to stand at least overnight at room temperature. The desorption efficiency results are in Table 1.

Table 1

Analytical - Desorption Efficiencies (THF)

Level	Weight of Glycidol Taken (mg)	Desorption Efficiency (Mean of Six Analyses)	Time on Charcoal (Hours)
0.5X	3.80	0.824	40
1.0X	7.48	0.861	15
2.0X	14.97	0.836	21

Loss of glycidol was suspected since the desorption efficiency of the 2.0X level was lower than the 1.0X level.

A study of milligrams of glycidol measured versus time on charcoal was then carried out. Charcoal tubes were spiked with 6.7 and 13.7 microliters of glycidol, and they were allowed to stand at room temperature. Similar spiked tubes were refrigerated at 4°C. Milligrams of glycidol were measured, after increasing passages of time using THF as the desorption solvent. Results are given in Table 2. Each numerical result is the average of two identically spiked charcoal tubes.

Table 2

Comparison of Recoveries (Desorption Efficiencies) of Refrigerated and Non-Refrigerated Samples of Glycidol

		Refrigerated Samples (4°C)			Non-Refrigerated Samples (25°C)		
µl taken	mg taken	mg found	time on charcoal (hr)	Recovery (%)	mg found	time on charcoal (hr)	Recovery (%)
6.7	7.48	-	-	-	6.80	6	90.9
"	"	-	-	-	6.63	7	88.6
"	"	6.14	18	82.1	6.44	15	86.1
"	"	6.77	42	90.5	5.41	42	72.3
"	"	5.98	91	79.9	5.10	87	68.2
"	"	6.15	115	82.2	3.77	111	50.4
"	"	6.31	185	84.4	3.99	137	53.3
13.4	14.97	14.37	15	96.0	13.32	15	89.0
"	"	13.51	63	90.2	9.04	63	60.4

The amount of glycidol found decreased as the time on the charcoal at 25°C increased. When the tubes were stored at 4°C, this decrease was not observed. The recovery (desorption efficiency) of glycidol was measured after the spiked charcoal tubes were refrigerated overnight. The generated samples of glycidol were also refrigerated overnight before analysis. Results are given in the laboratory data section of this report.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.016$ $\overline{CV}_2 = 0.062$ $\overline{CV}_T = 0.080$

The average recovery at the OSHA standard level was 96.9%.

Data Sheet: Glycidol S70

Analysis

(Refrigerated)

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
3.80	3.33	0.876	7.48	7.02	0.939	14.97	14.05	0.939
3.80	3.45	0.908	7.48	6.99	0.934	14.97	14.01	0.936
3.80	3.34	0.879	7.48	6.97	0.932	14.97	14.08	0.941
3.80	3.35	0.882	7.48	6.95	0.929	14.97	13.96	0.933
3.80	3.31	0.871	7.48	6.73	0.900	14.97	13.92	0.930
3.80	3.36	0.884	7.48	6.73	0.900	14.97	14.34	0.958
n=		6			6			6
mean		0.883			0.922			0.940
std dev		0.013			0.018			0.010
CV_1		0.015			0.020			0.011

$\overline{CV}_1$ 0.016

$\overline{CV}_{A+\overline{DE}}$ 0.017

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Glycidol S70

Sampling and Analysis

(Refrigerated)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m *	mg/cu m	Recovery
0.5S	3.16	3.61	50.5	71.5	72.8	
	3.46	3.92	51.8	75.7	72.8	
	3.32	3.77	51.4	73.3	72.8	
	3.40	3.85	51.9	74.2	72.8	
	3.30	3.75	52.1	72.0	72.8	
	3.35	3.80	51.5	73.8	72.8	
			n = 6			
			mean	73.4		100.8
			std dev	1.5		
			CV_2	0.020		
1S	6.45	7.01	49.0	143.1	150.2	
	7.09	7.68	49.0	156.7	150.2	
	6.63	7.20	47.8	150.6	150.2	
	6.14	6.70	49.2	136.2	150.2	
	6.52	7.09	48.4	146.5	150.2	
	6.12	6.68	47.5	140.6	150.2	
			n = 6			
			mean	145.6		96.9
			std dev	7.3		
			CV_2	0.050		
2S	13.34	14.22	49.9	285.0	310	
	13.46	14.33	49.7	288.3	310	
	12.71	13.56	50.0	271.2	310	
	13.81	14.71	49.9	294.8	310	
	10.72	11.45	50.3	227.6	310	
	(Sample was lost.)					
			n = 5			
			mean	273.4		88.2
			std dev	27.0		
$\overline{CV}_2$ 0.062			CV_2	0.099		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Methylal (Dimethoxymethane), No. S71
OSHA Standard:	3110 mg/cu m
Chemical used for validation:	Methylal, Lot 1-7278 J.T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of methylal in air is described in NIOSH Method S71, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid methylal to represent 2 liter air samples. Samples of methylal in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of methylal in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 11 minutes). The "true" value for the concentration of methylal generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There was only one major modification made to P&CAM 127 which was to use hexane as the desorbing solvent instead of carbon disulfide. (See Discussion Section).

Generation

Samples of methylal in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 167.4 ml per minute, measured at 22°C, was bubbled through the methylal in the generator flask, which was maintained at a temperature of 22°C. After passing through the condenser, which was water cooled at 20.4°C, the methylal vapor was diluted to the 2X OSHA standard level with air added at a rate of 56.8 liters per minute measured at 22°C. Two further dilutions were made to obtain concentrations at the 1X and 0.5X OSHA levels.

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 2). The three

sampling chambers were monitored alternately during the time the samples were being collected. Samples were collected for 11 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 20 minutes when a concentration of 6250 mg/cu m was sampled at a rate of 0.183 liter per minute.

Discussion

It was necessary to choose another eluent for the method, because methylal in carbon disulfide gave a very small poorly shaped peak on the gas chromatogram. This peak was not useful for quantitative measurement of methylal. The GC conditions used were as follows:

1. 50 ml/minute (60 psig) nitrogen carrier gas flow
2. 65 ml/minute (24 psig) hydrogen gas flow to detector
3. 500 ml/minute (50 psig) air flow to detector
4. 190°C injector temperature
5. 250°C manifold temperature
6. 195°C column temperature

A 4-ft X 1/4-in stainless steel column packed with 50/80 mesh Porapak Q was used.

Carbon disulfide, dried over magnesium sulfate, was tested. There was no improvement in the peak shape.

Methylal in hexane was tested, and a nicely shaped methylal peak was observed on the gas chromatogram. Hexane was therefore used as the eluent for the method.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.017$ $\overline{CV}_2 = 0.032$ $\overline{CV}_T = 0.060$

The average recovery at the OSHA standard level was 104.6%.

Data Sheet: Methylal S71

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
3.082	2.388	0.775	6.16	4.98	0.808	12.33	10.66	0.865
3.082	2.424	0.787	6.16	4.99	0.810	12.33	10.86	0.881
3.082	2.424	0.787	6.16	4.99	0.810	12.33	11.11	0.901
3.082	2.290	0.743	6.16	5.00	0.812	12.33	10.83	0.878
3.082	2.438	0.791	6.16	5.03	0.817	12.33	10.84	0.879
3.082	2.369	0.769	6.16	4.89	0.794	12.33	10.66	0.865

n=	6	6	6
mean	0.775	0.808	0.878
std dev	0.018	0.008	0.013
CV_1	0.023	0.010	0.015

$\overline{CV}_1$ 0.017

$\overline{CV}_{A+\overline{DE}}$ 0.018

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Methylal S71

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m *	mg/cu m	Recovery
0.5S	3.110	3.95	2.313	1708	1623	
	2.876	3.67	2.124	1728	1623	
	2.639	3.39	2.091	1621	1623	
	2.858	3.65	2.135	1710	1623	
	2.898	3.70	2.235	1655	1623	
	(Sample was lost.)					
			n = 5			
			mean	1684		103.8
			std dev	45		
			CV_2	0.027		
1S	5.17	6.33	1.946	3250	3210	
	4.30	5.34	1.712	3120	3210	
	5.56	6.76	1.946	3470	3210	
	5.39	6.57	1.879	3500	3210	
	5.07	6.22	1.846	3370	3210	
	5.11	6.27	1.824	3440	3210	
			n = 6			
			mean	3360		104.6
			std dev	147		
			CV_2	0.044		
2S	11.62	13.22	2.024	6530	6300	
	12.53	14.19	2.091	6790	6300	
	11.80	13.41	2.057	6520	6300	
	12.23	13.88	2.057	6750	6300	
	12.31	13.96	2.068	6750	6300	
	12.07	13.72	2.057	6670	6300	
			n = 6			
			mean	6670		105.8
			std dev	118		
$\overline{CV}_2$	0.032		CV_2	0.018		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Phenyl Ether, No. S72

OSHA Standard: 7 mg/cu m

Chemical used for validation: Phenyl Ether, Lot 233603
J.T. Baker Chemical Company

Procedure

The procedure for collection and analyzing concentrations of phenyl ether in air is described in NIOSH Method S72, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of phenyl ether to represent 10 liter air samples. Samples of phenyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of phenyl ether in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.6 minutes).

Modifications

Only one major modification to the general P&CAM 127 method was made. The volume of liquid phenyl ether equivalent to that which would be collected on the charcoal tubes was less than 1 microliter at the 0.5X level. Therefore, a hexane solution containing 17.3 mg/ml was used to apply the phenyl ether to the charcoal for the desorption efficiency tests.

Generation

Samples of phenyl ether in air were generated by the procedure described in the Backup Data Report for 2-butoxy ethanol (Reference No. 1,2). The nitrogen flow rate in the vapor generator was 176 ml/minute at 24°C; the dilution air flow was 45.5 liter/minute at 24°C; the bath temperature was 66°C.

The concentration of phenyl ether at 14 mg/cu m, which corresponds to 2 times the OSHA standard, was too low to be measured by gas chromatography of air samples taken directly from the 2X chamber. Also, since the volume of liquid phenyl ether which would be required to prepare a 10 liter bag sample was less than 1 microliter, bag standards could not be prepared and neither the gas chromatograph nor the total hydrocarbon analyzer could be calibrated. However, the constancy of the concentration of phenyl ether in the generator could be monitored using a Beckman Model 402 total hydrocarbon analyzer

during the sample collection and the breakthrough experiments. The concentration in the 2X chamber deviated less than ± 5% from the average level throughout the sampling and the breakthrough experiments.

Since the concentration of phenyl ether at the 2X level could not be measured directly in the generator with either the gas chromatograph or the hydrocarbon analyzer, it was necessary to use an indirect method based on collection efficiency. The method chosen is based on measuring the amount of phenyl ether collected on each of two sections of the charcoal tube. In this method, it must be demonstrated that as little as 1% of the phenyl ether in the sample could be found if it were present on the backup section of the charcoal tube. Therefore, the D.E. of phenyl ether at a low level was determined by spiking 50 mg of charcoal with 6.97 μg of phenyl ether. For comparison, 0.1381 mg of phenyl ether had been spiked on 100 mg of charcoal to determine the D.E. at 2 times the OSHA standard. In all cases, the phenyl ether was desorbed with 0.5 ml of CS_2. The D.E. data at this low level are reported in Table 1. The sensitivity of the GC method was such that as little as 0.7 μg of phenyl ether in 0.5 ml CS_2 could have been detected.

Table 1

DESORPTION EFFICIENCIES AT A LOW LEVEL

μg taken	μg found	D.E.
6.97	5.54	0.79
6.97	5.72	0.82
6.97	5.42	0.78
6.97	6.18	0.89
6.97	5.42	0.78
6.97	5.14	0.74
	mean	0.80

Mean values of D.E. at the 0.5X, 1X, and 2X levels were found to be 0.890, 0.902, and 0.913, respectively. Thus, it was established that the D.E. value at the 7 μg level was adequate for analysis of the backup section of the charcoal tube in determining collection efficiency.

The backup section of each tube for a 10 liter sample collected from the 2X chamber was desorbed with 0.5 ml of CS_2 and analyzed; no phenyl ether was detected. As a result of these experiments, the collection efficiency of the charcoal tubes for phenyl ether was found to be 1.00 ± 0.01.

The mg/cu m taken for each generated level was then calculated as follows. The dilution ratios of the generator were calculated from the measured flow rates through each critical orifice in the generator system (Reference No. 4). The concentration in the 1X chamber is 0.500 times the concentration in the 2X chamber; the concentration in the

0.5X chamber is 0.250 times the concentration in the 2X chamber. The taken mg/cu m value for the 2X chamber concentration was estimated by calculating the average of the mean of the found concentrations in chamber weighted by the dilution factor for each chamber. Thus,

$$2X \text{ taken} = \frac{1}{3}\left(\frac{2X \text{ found}}{1.00} + \frac{1X \text{ found}}{0.500} + \frac{0.5X \text{ found}}{0.250}\right)$$

$$= \frac{1}{3}\left(\frac{13.10}{1.00} + \frac{6.69}{0.500} + \frac{3.36}{0.250}\right)$$

$$= 13.30 \text{ mg/cu m}$$

where 2X taken refers to the taken concentration in the 2X chamber and 2X, 1X, and 0.5X found refer to the mean of the found concentration in the three chambers, all expressed in mg/cu m. Then, using the known dilution factors, the taken concentrations are 6.65 mg/cu m in the 1X chamber and 3.32 mg/cu m in the 0.5X chamber.

Samples of phenyl ether were collected for 54.6 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate.)

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted. A total hydrocarbon analyzer was used as described above to monitor the effluent concentration of 6 tubes containing only the 100 mg section of charcoal, after the concentration of 13.3 mg/cu m had been established by analysis of charcoal tubes. Less than 2% of the generated concentration of 13.3 mg/cu m was present in the effluent after 4 hours sampling at an average rate of 0.185 liter per minute, indicating that the capacity of the front section of a charcoal tube is greater than 0.6 mg of phenyl ether. The results of the breakthrough test confirm excellent collection efficiency.

Discussion

The results described in NIOSH Method S73 for phenyl ether-biphenyl mixture suggest that a valid method could also be obtained using silica gel tubes, a 10 liter air sample, and benzene as the desorption solvent (Reference No. 3).

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$$\overline{CV}_1 = 0.017 \qquad \overline{CV}_2 = 0.048 \qquad \overline{CV}_T = 0.070$$

The average recovery at the OSHA standard level was 100.6%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Phenyl Ether S72

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.0345	0.0306	0.887	0.0690	0.0616	0.893	0.1381	0.1270	0.920
0.0345	0.0306	0.887	0.0690	0.0626	0.907	0.1381	0.1278	0.925
0.0345	0.0305	0.884	0.0690	0.0607	0.880	0.1381	0.1226	0.888
0.0345	0.0304	0.881	0.0690	0.0618	0.896	0.1381	0.1270	0.920
0.0345	0.0304	0.881	0.0690	0.0638	0.925	0.1381	0.1268	0.918
0.0345	0.0318	0.922	0.0690	0.0627	0.909	0.1381	0.1253	0.907

n =	6	6	6
mean	0.890	0.902	0.913
std dev	0.016	0.016	0.014
CV_1	0.018	0.018	0.015

$\overline{CV}_1$ 0.017

$\overline{CV}_{A+\overline{DE}}$ 0.018

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Phenyl Ether S72

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.0320	0.0355	10.44	3.40	3.32	
	0.0326	0.0361	10.98	3.29	3.32	
	0.0330	0.0366	10.27	3.56	3.32	
	0.0355	0.0394	11.37	3.46	3.32	
	0.0294	0.0326	10.82	3.01	3.32	
	0.0323	0.0358	10.49	3.41	3.32	
			n = 6			
			mean	3.36		101.2
			std dev	0.19		
			CV_2	0.056		
1S	0.0535	0.0593	8.42	7.04	6.65	
	0.0532	0.0590	9.07	6.50	6.65	
	0.0550	0.0610	9.56	6.38	6.65	
	0.0575	0.0637	9.24	6.89	6.65	
	0.0578	0.0641	9.56	6.70	6.65	
	0.0536	0.0594	8.96	6.63	6.65	
			n = 6			
			mean	6.69		100.6
			std dev	0.24		
			CV_2	0.036		
2S	0.1131	0.1254	9.95	12.60	13.30	
	0.1170	0.1297	10.11	12.83	13.30	
	0.1138	0.1262	10.16	12.42	13.30	
	0.1175	0.1303	9.67	13.48	13.30	
	0.1261	0.1453	10.27	14.15	13.30	
	0.1197	0.1327	10.11	13.13	13.30	
			n = 6			
			mean	13.10		98.7
			std dev	0.64		
$\overline{CV}_2$	0.048		CV_2	0.049		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, 2-Butoxy Ethanol, No. S76, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Phenyl Ether-Biphenyl Mixture, No. S73, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Phenyl Ether-Biphenyl Mixture, No. S73
OSHA Standard:	7 mg/cu m
Chemical used for validation:	Phenyl Ether, Lot 233603 J. T. Baker Chemical Company Biphenyl, Lot 21 Matheson, Coleman and Bell

Procedure

The procedure for collecting and analyzing concentrations of phenyl ether-biphenyl mixture in air is described in NIOSH Method S73, which has been adapted from P&CAM 127. The phenyl ether-biphenyl mixture was prepared by dissolving 53 g of biphenyl in 147 g of melted phenyl ether. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150 mg portions of silica gel* with the appropriate amounts of phenyl ether-biphenyl mixture to represent 10 liter air samples. The desorption efficiencies (D.E.) for phenyl ether and biphenyl were determined separately and are reported in the Analysis Data Sheets (Tables 6 to 10) attached to this report. Samples of phenyl ether-biphenyl mixture in air were generated and collected in silica gel tubes. The analytes were desorbed with benzene and analyzed by gas chromatography using conditions which allowed measurement of both components separately. The amounts measured were corrected for D.E. by use of the appropriate D.E. curve, to determine corrected mg for each. The sampling and analysis data for phenyl ether and biphenyl separately, and for the phenyl ether-biphenyl mixture are reported in the Sampling and Analysis Data Sheets which are attached. The concentration in air "found" for each component was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.7 minutes). The concentration "found" for the mixture is the sum of the "found" concentrations of the two components.

Modifications

Three major modifications were made to P&CAM 127. The samples were collected on silica gel tubes. A hexane solution of the analyte was used for spiking sorbent in the D.E. tests because of the low amounts required. The analyte was desorbed using benzene. The reasons for these modifications are discussed in the Desorption Efficiency section of this report.

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* Silica gel tubes were obtained from Environmental Compliance Corp., Venetia, Pa., Catalog 226-10.

Generation

Samples of the phenyl ether-biphenyl mixture were generated using a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950) to avoid fractionating the mixture during vaporization. A 2-ml syringe was filled with the mixture and placed in the syringe-drive pump. A 12-inch long stainless steel needle was attached to the syringe. The other end of the needle passed through a rubber septum into a heated glass tube maintained at 280°C. The tube was packed with glass beads to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of N_2 at 1.94 liter/minute and diluted with air at 52.1 liter/minute immediately after the heated zone. The dilution system is described in Reference 1.

The concentration in the 2X, 1X, and 0.5X sampling chambers could be estimated from the rate of delivery of the phenyl ether-biphenyl mixture by the syringe drive, the total volume of air plus nitrogen into which the mixture was evaporated, and the known dilution ratios of the system. This estimate was used to "set" the concentration at a level near the desired concentrations. The "true" concentration was determined as described below.

An indirect method based on analysis of collected samples and collection efficiency of the silica gel for this mixture was used to determine the "true" concentration of material in the sampling chambers. The usual technique of calibration and measurement by using "bag" standards in conjunction with either a total hydrocarbon analyzer or a gas chromatograph which are available for monitoring the sampling chambers was not feasible because of the small amount of the mixture required to prepare a "bag" standard (less than 1 µl of the mixture for a 10 liter bag standard). (See Reference 1 for information on the sample generation system.) The constancy of the concentration of material in the sampling chamber could be monitored using a Beckman Model 402 total hydrocarbon analyzer.

This indirect method of determining the "true" concentration of material in the sampling chamber is based on the following:

1. Demonstration by the appropriate tests that if a small amount of the mixture is collected on the sorbent it can be successfully desorbed and measured.

2. Determination of the sensitivity of measurement for the desorbed material, i.e., determination of the smallest amount which can be detected.

3. Desorption and analysis of the backup portions of collection tubes to verify that the sampled material has been retained on the front section of the tube, using the information from the above tests to set the limits of measurement.

4. Use of the averages of the found concentrations of the set of collected samples to calculate the "true" concentrations, after satisfactorily demonstrating by the above measurements that all the material which was sampled through the collection tube was retained on the front section.

To verify that a small amount of the mixture could be desorbed from silica gel and measured, a desorption efficiency test was done by spiking 150 mg of silica gel with 7 μg of the mixture (using 4 μl of a hexane solution containing 1.75 mg/l). For comparison, 140 μg is used for D.E. at the 2X level. One-half ml of benzene was used as the solvent. The data are summarized in Table 1. The sensitivity of the GC method was such that .035 μg of the mixture could be detected.

Table 1

DESORPTION EFFICIENCIES OF THE SUM OF PHENYL ETHER AND BIPHENYL AT A LOW LEVEL

mg taken	mg found	D.E.
0.00700	0.00618	0.883
0.00700	0.00624	0.892
0.00700	0.00618	0.883
	mean	0.889

Thus, it was established that the D.E. value at this low level was adequate for analysis of the backup section of the silica gel tubes in determining collection efficiency.

Next, the backup sections of the six silica gel tubes used for the breakthrough test were examined. (See Breakthrough Test discussion which follows.) The approximate 75 mg of silica gel on the backup section was desorbed with 0.25 ml of benzene to maintain the same ratio of solvent to sorbent as used in the D.E. tests. None of the test mixture was found on any of the six backup sections. Since breakthrough had been conducted for a period of 4 hours at a concentration of 14.9*mg/cu m and sampling rate of 0.185 liter per minute, 0.66 mg of the mixture was introduced into the front section of the silica gel tube. Using the results of the D.E. test and the

* See calculation on page S73-4 for 2X taken.

known sensitivity of the GC for the mixture, it was determined that the maximum amount of mixture that could have been on the backup section was 2 μg. This 2 μg represents less than 0.3% of the 0.66 mg mixture that was sampled during the breakthrough test. From this result, the conclusion was made that the collection efficiency of the silica gel was 1.00 ± 0.01.

The mg/cu m taken for phenyl ether and biphenyl separately for each generated level was then calculated as follows. The dilution ratios of the generator were calculated from the measured flow rates through each critical orifice in the generator system (Reference No. 1). The concentration in the 1X chamber is 0.500 times the concentration in the 2X chamber; the concentration in the 0.5X chamber is 0.250 times the concentration in the 2X chamber. The taken mg/cu m value for the 2X chamber concentration was estimated by calculating the average of the mean of the found concentrations in chamber weighted by the dilution factor for each chamber. Thus,

$$2X \text{ taken} = \frac{1}{3}\left(\frac{2X \text{ found}}{1.00} + \frac{1X \text{ found}}{0.500} + \frac{0.5X \text{ found}}{0.250}\right)$$

where 2X taken refers to the taken concentration in the 2X chamber and 2X, 1X, and 0.5X found refer to the mean of the found concentration in the three chambers, all expressed in mg/cu m. Then, using the known dilution factors, the taken concentrations in the 1X and 0.5X chambers were calculated. The taken value in mg/cu m for the mixture is the sum of the taken values for phenyl ether and biphenyl.

Table 2

CHAMBER CONCENTRATIONS (mg/cu m)

	Phenyl Ether	Biphenyl	Mixture
2X Chamber	11.10	3.77	14.87
1X Chamber	5.55	1.885	7.44
0.5X Chamber	2.775	0.942	3.72

Samples of phenyl ether-biphenyl were collected for 54.7 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate.)

Breakthrough

Breakthrough tests are usually conducted by comparison of the response of a total hydrocarbon analyzer to the material in the test chamber and to the material which has passed through the tubes used for testing. When the response of the material passing through the tubes reaches 5% of the response to the material in the chamber, this time is noted as the breakthrough time. The volume sampled is then found by multiplying the sampling rate by the breakthrough time.

Since the phenyl ether-biphenyl mixture concentration at the 2X OSHA level is only 14 mg/cu m, the total hydrocarbon analyzer used to monitor the chamber concentration did not have the required sensitivity to measure at 5% of this level. An alternate experiment was done using the silica gel tubes containing both front and backup sections. This experiment was based on the premise that if no material was found on the backup sections of the tubes, then breakthrough did not occur. Six tubes in the 2X chamber were sampled for 4 hours at an average rate of 0.185 liter per minute. After the test was completed the backup sections of the tubes were examined. The Generation section of this report describes the experiments conducted, and the results.

No material was found on any of the six backup sections.

The concentration of the chamber for the breakthrough test is the same as the concentration for sample generation, both tests having been conducted consecutively without changing conditions. The 2X chamber was monitored continuously during the 4 hour breakthrough tests using the total hydrocarbon analyzer and did not change within $\pm$ 5%.

In summary, it was found that the front section of the silica gel tubes retained 0.66 mg of the phenyl ether-biphenyl mixture introduced into the tube when sampling at a rate of 0.185 liter per minute for 4 hours from a concentration of 14.87 mg/cu m. Thus, the capacity of a silica gel tube is at least, and possibly much greater than, 0.7 mg of the eutectic mixture. The volume sampled was more than 4 times the 10 liter volume specified in NIOSH Method S73.

Desorption Efficiency

Phenyl ether can be collected on activated charcoal (SKC Lot 105) and desorbed with a D.E. of 0.902 at 1 times the OSHA standard (0.069 mg taken) using CS_2 (Reference 2). However, biphenyl could not be desorbed with an adequate efficiency from SKC Lot 105 charcoal using CS_2, benzene, or methylene chloride (Reference 3). Therefore, the initial experiments were directed towards finding a satisfactory sorbent to desorb biphenyl. Additional solvents for desorption from charcoal (Table 3) and alternative sorbents (Table 4) were tested. In addition, Tenax GC and molecular sieve 13X (Applied Science Laboratories, Inc., State College, Penna., 30/60 mesh, Lot 112271) were evaluated. Tenax GC dissolved in benzene; molecular sieve 13X discolored in benzene; both were judged to be unsatisfactory. Using benzene as the desorption solvent, the SKC silica gel and Chromosorb 101 (washed with benzene and dried in a hood before use) were satisfactory sorbents. Silica gel was selected for further studies.

Table 3

D.E. FOR BIPHENYL ON ACTIVATED CHARCOAL*

Solvent (0.5 ml each)	mg taken	mg found	D.E.
CS_2	0.0321	0.0102	0.318
CS_2	0.2406	0.1191	0.495
THF	0.2406	0.005	0.02
Benzene	0.2406	0.1174	0.488
Methanol	0.2406	0	0

* SKC Lot 105

The liquid volume of phenyl ether-biphenyl mixture equivalent to that which would be collected on the silica gel tubes was less than 1 microliter at 0.5 times the OSHA standard. Therefore, a hexane solution containing 17.5 mg/ml was prepared, and 2, 4, and 8 µl aliquots were used to apply the phenyl ether-biphenyl mixture to the silica gel for the desorption efficiency tests. The preliminary data showed that CS_2 was not a satisfactory solvent for desorption because the D.E. was 0.355 (Table 4). Therefore, the analyte was desorbed with 0.5 ml benzene using the same technique used for samples collected on activated charcoal.

Table 4

PRELIMINARY MEASUREMENTS OF

DESORPTION EFFICIENCIES FOR CHROMOSORB 101 AND SILICA GEL

		Phenyl ether			Biphenyl		
Sorbent	Solvent (0.5 ml)	mg taken**	mg found	D.E.	mg taken**	mg found	D.E.
Chromosorb 101*	Benzene	0.0515	0.2547	1.062	0.01855	0.01558	0.840
Silica Gel	Benzene	0.0515	0.0496	0.963	0.01855	0.02003	1.080
Silica Gel	CS_2	0.0515	0.0110	0.214	0.01855	0.00658	0.355

* Prewashed with benzene and dried in a hood.

** At the 1X level and a 10 liter sample, 0.0700 mg phenyl ether-biphenyl mixture would be collected. The mg taken were calculated from the composition of the mixture.

Discussion

In order to obtain well-resolved peaks for biphenyl and phenyl ether on the gas chromatograph, it was necessary to use a 10-ft X 1/8-inch, 5% OV-17 on Chrom W column, under the operating conditions described in NIOSH Method S73.

The results described in NIOSH Method S73 for phenyl ether-biphenyl mixture suggest that a valid method for phenyl ether and a valid method for biphenyl could be obtained using silica gel tubes, a 10 liter air sample, and benzene as the desorption solvent.

This method for phenyl ether-biphenyl eutectic mixture is directly applicable to each component separately.

Precision and Accuracy

The data for D.E. and sampling and analysis are presented for each component in the mixture, since the OV-17 column gave separate peaks for phenyl ether and biphenyl and each component could be analyzed separately. These data are presented in Tables 6 through 9. The data for the phenyl ether-biphenyl mixture are reported in Table 10. The mg/cu m found values in Table 10 for each individual sample are the sum of the corresponding values in Tables 7 and 9. The mg/cu m taken values are the corresponding values from Table 2.

The Coefficients of Variation, $\overline{CV}_1$, $\overline{CV}_2$, and $\overline{CV}_T$ for each component in the mixture as well as $\overline{CV}_2$ for the eutectic mixture, were calculated by the methods described in Reference No. 4.

The values of $(CV_1)_m$ and $(\overline{CV}_1)_m$ were estimated from the following equations, using the means and standard deviations of the D.E. data from Tables 6 and 8.

$$(CV_1)^2_{M_i} = \frac{\sigma^2_{PE} + \sigma^2_B}{(\overline{X}_{PE} + \overline{X}_B)^2}$$

$$(\overline{CV}_1)_M = \sqrt{\frac{\sum_i (n_i - 1)(CV_1)^2_{M_i}}{\sum_i (n_i - 1)}}$$

where subscripts PE, B, and M refer to phenyl ether, biphenyl, and the eutectic mixture respectively, and i refers to the number of levels. In general, the equations given in Busch's memo of November 8, 1974 (Reference No. 5) can be transformed in the following way:

(1) $\overline{CV}^2_{A+\overline{DE}} = \overline{CV}^2_1 (1 + 1/6)$

(2) $\overline{CV}^2_S = \overline{CV}^2_2 - \overline{CV}^2_1$

(3) $\overline{\overline{CV}}^2_T = \overline{CV}^2_{A+\overline{DE}} + \overline{CV}^2_S$

By substituting equations 1 and 2 into equation 3:

$$\overline{CV}^2_T = \overline{CV}^2_1 (1 + 1/6) + \overline{CV}^2_2 - \overline{CV}^2_1 + CV^2_p$$

$$\overline{CV}^2_T = 1/6\ \overline{CV}^2_1 + \overline{CV}^2_2 + CV^2_p$$

where $CV_p = 0.05$ (pump error)

Then

$$(CV_T)_M = \left[1/6\ (\overline{CV}_1)^2_M + (\overline{CV}_2)^2_M + CV^2_p \right]^{\frac{1}{2}}$$

The estimates of these statistics may be found in Table 5.

Table 5

COEFFICIENTS OF VARIATION

	$\overline{CV}_1$	$\overline{CV}_2$	$\overline{CV}_T$
Phenyl ether	0.038	0.070	0.087
Biphenyl	0.046	0.086	0.101
Eutectic mixture	0.030	0.073	0.089

The average recovery at the OSHA standard level for the eutectic mixture was apparently 91.0%. However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

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Table 6

Data Sheet: Phenyl Ether in Eutectic

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.02573	0.02491	0.968	0.0515	0.0467	0.907	0.1029	0.1061	1.031
0.02573	0.02394	0.930	0.0515	0.0485	0.942	0.1029	0.1059	1.029
0.02573	0.02428	0.944	0.0515	0.0510	0.990	0.1029	0.1076	1.046
0.02573	0.02209	0.859	0.0515	0.0496	0.963	0.1029	0.1011	0.983
0.02573	0.02463	0.957	0.0515	0.0514	0.998	0.1029	0.1002	0.974
0.02573	0.02372	0.922	0.0515	0.0518	1.006	0.1029	0.1014	0.985
n =		6			6			6
mean		0.930			0.968			1.008
std dev		0.039			0.038			0.031
$CV_1 = (CV_1)_{PE}$		0.042			0.039			0.031

$$\overline{CV}_1 = (\overline{CV}_1)_{PE} = 0.038$$

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate corr. mg in the Sampling and Analysis table for phenyl ether in eutectic.

Table 7

Data Sheet: Phenyl Ether in Eutectic

Sampling and Analysis

Test Level	Found					Taken
	Sample No.	mg	Corr mg	Liters	mg/cu m*	mg/cu m
0.5S	1	0.03300	0.0348	10.50	3.314	2.775
	2	0.03051	0.0324	10.99	2.948	2.775
	3	0.02601	0.0279	10.28	2.714	2.775
	4	0.02981	0.0317	11.38	2.786	2.775
	5	0.02715	0.0290	10.45	2.775	2.775
	6	0.02924	0.0311	10.83	2.872	2.775
				n = 6		
				mean	2.902	
				std dev	0.218	
				$CV_2 = (CV_2)_{PE}$	0.075	
1S	7	0.0478	0.0493	9.57	5.15	5.55
	8	0.0479	0.0494	8.97	5.51	5.55
	9	0.0396	0.0413	8.42	4.90	5.55
	10	0.0449	0.0466	9.57	4.87	5.55
	11	0.0371	0.0389	9.08	4.28	5.55
	12	0.0459	0.0475	9.24	5.14	5.55
				n = 6		
				mean	4.98	
				std dev	0.41	
				$CV_2 = (CV_2)_{PE}$	0.082	
2S	13	0.1262	0.1240	10.12	12.25	11.10
	14	0.1260	0.1239	10.12	12.24	11.10
	15	(Sample was lost.)				
	16	0.1165	0.1152	10.12	11.38	11.10
	17	0.1139	0.1128	10.17	11.09	11.10
	18	0.1185	0.1170	9.96	11.75	11.10
				n = 5		
				mean	11.74	
				std dev	0.52	
$\overline{CV}_2 = (\overline{CV}_2)_{PE} = 0.070$				$CV_2 = (CV_2)_{PE}$	0.044	

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

Table 8

Data Sheet: Biphenyl in Eutectic

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.00928	0.00836	0.901	0.01855	0.01729	0.932	0.0371	0.0388	1.046
0.00928	0.00761	0.820	0.01855	0.01769	0.954	0.0371	0.0399	1.075
0.00928	0.00917	0.988	0.01855	0.01856	1.001	0.0371	0.0385	1.038
0.00928	0.00833	0.898	0.01855	0.01850	0.997	0.0371	0.0355	0.957
0.00928	0.00864	0.931	0.01855	0.01869	1.008	0.0371	0.0369	0.995
0.00928	0.00851	0.917	0.01855	0.01846	0.995	0.0371	0.0372	1.003
n =		6			6			6
mean		0.909			0.981			1.019
std dev		0.055			0.031			0.042
$CV_1 = (CV_1)_B$		0.060			0.032			0.041

$$\overline{CV}_1 = (\overline{CV}_1)_B = 0.046$$

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate corr. mg in the Sampling and Analysis table for biphenyl in eutectic.

Table 9

Data Sheet: Biphenyl in Eutectic

Sampling and Analysis

Test Level	Found					Taken
	Sample No.	mg	Corr mg	Liters	mg/cu m	mg/cu m
0.5S	1	0.01081	0.01159	10.50	1.104	0.942
	2	0.00989	0.01069	10.99	0.973	0.942
	3	0.00853	0.00940	10.28	0.914	0.942
	4	0.00920	0.01004	11.38	0.882	0.942
	5	0.00822	0.00910	10.45	0.871	0.942
	6	0.00965	0.01049	10.83	0.969	0.942
				n = 6		
				mean	0.952	
				std dev	0.086	
				$CV_2 = (CV_2)_B$	0.090	
1S	7	0.01769	0.01809	9.57	1.890	1.885
	8	0.01767	0.01809	8.97	2.017	1.885
	9	0.01492	0.01548	8.42	1.838	1.885
	10	0.01444	0.01503	9.57	1.570	1.885
	11	0.01335	0.01399	9.08	1.541	1.885
	12	0.01710	0.01754	9.24	1.898	1.885
				n = 6		
				mean	1.792	
				std dev	0.193	
				$CV_2 = (CV_2)_B$	0.108	
2S	13	0.0419	0.0412	10.12	4.07	3.77
	14	0.0420	0.0413	10.12	4.08	3.77
	15	0.0256	0.0255	10.29	2.48*	3.77
	16	0.0396	0.0389	10.12	3.84	3.77
	17	0.0390	0.0383	10.17	3.77	3.77
	18	0.0393	0.0386	9.96	3.88	3.77
				n = 5		
				mean	3.93	
				std dev	0.14	
$\overline{CV}_2 = (\overline{CV}_2)_B = 0.086$				$CV_2 = (CV_2)_B$	0.036	

* Deleted as an outlier as described in Reference No. 6.

Table 10

Data Sheet: Phenyl Ether-Biphenyl Mixture S73

Sampling and Analysis

Test Level	Sample No.	Found mg/cu m*	Taken mg/cu m	Recovery
0.5S	1	4.42	3.72	
	2	3.92	3.72	
	3	3.64	3.72	
	4	3.66	3.72	
	5	3.65	3.72	
	6	3.84	3.72	
	n=6			
	mean	3.86		103.8
	std dev	0.30		
	$CV_2=(CV_2)_M$	0.078		
1S	7	7.04	7.44	
	8	7.53	7.44	
	9	6.75	7.44	
	10	6.44	7.44	
	11	5.83	7.44	
	12	7.03	7.44	
	n=6			
	mean	6.77		91.0
	std dev	0.58		
	$CV_2 = (CV_2)_M$	0.086		
2S	13	16.32	14.87	
	14	16.32	14.87	
	15	(Incomplete data for this sample.)		
	16	15.23	14.87	
	17	14.86	14.87	
	18	15.62	14.87	
	n=5			
	mean	15.67		105.4
	std dev	0.65		
	$CV_2 = (CV_2)_M$	0.041		

$\overline{CV_2} = (\overline{CV_2})_M = 0.073$

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. NIOSH Method S72, and Backup Data Report, Phenyl Ether, No. S72, prepared under NIOSH Contract CDC-99-74-45.

3. Failure Report, Biphenyl, S29, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. NIOSH Memo to Deputy Director, DLCD, from Chief, Statistical Services, DLCD, entitled "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45," November 8, 1974.

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Phenyl Glycidyl Ether, No. S74
OSHA Standard:	60 mg/cu m
Chemical used for validation:	Phenyl Glycidyl Ether, Lot 25-4 Electron Microscopy Sciences

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of phenyl glycidyl ether in air is described in NIOSH Method S74, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid phenyl glycidyl ether to represent 50 liter air samples. Samples of phenyl glycidyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The concentration of phenyl glycidyl ether in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 53.5 minutes). The "true" value for the concentration of phenyl glycidyl ether generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration, as described in Reference No. 1.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of phenyl glycidyl ether in air were generated by the procedure described in the Backup Data Report for 2-butoxy ethanol (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions for Phenyl Glycidyl Ether

Nitrogen flow rate	40.8 ml/minute at 22°C
Dilution air flow rate	42.5 liters/minute at 22°C
Bath temperature	31°C

A Beckman 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 1). Samples were collected for 53.5 minutes at a rate of approximately 1.0 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene. (Reference No. 1). Less than 5% of the generated concentration of 112 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.93 liter per minute, indicating a capacity of at least 25 mg of phenyl glycidyl ether in the charcoal tube.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.022$ $\overline{CV}_2 = 0.025$ $\overline{CV}_T = 0.057$

The average recovery at the OSHA standard level was 91.2%.

Data Sheet: Phenyl Glycidyl Ether S74

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.553	1.520	0.979	2.994	2.917	0.974	5.99	5.78	0.965
1.553	1.480	0.953	2.994	2.879	0.962	5.99	5.73	0.956
1.553	1.528	0.984	2.994	2.981	0.996	5.99	6.03	1.007
1.553	1.522	0.980	2.994	2.820	0.942	5.99	6.02	1.005
1.553	1.556	1.002	2.994	2.881	0.962	5.99	6.04	1.008
1.553	1.580	1.017	2.994	2.822	0.942	5.99	6.05	1.010
n=		6			6			6
mean		0.986			0.963			0.992
std dev		0.022			0.020			0.024
CV_1		0.022			0.021			0.024

$\overline{CV}_1$ 0.022

$\overline{CV}_{A+\overline{DE}}$ 0.024

A desorption efficiency of 0.980 was used for calculation of the corr. mg in the Sampling and Analysis table at all three levels.

Data Sheet: Phenyl Glycidyl Ether S74

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	1.428	1.457	52.0	28.02	30.72	
	1.444	1.473	50.5	29.17	30.72	
	1.451	1.481	51.8	28.59	30.72	
	1.442	1.471	52.1	28.23	30.72	
	1.371	1.399	51.4	27.22	30.72	
	1.465	1.495	51.5	29.03	30.72	
			n = 6			
			mean	28.38		92.4
			std dev	0.72		
			CV_2	0.025		
1S	2.564	2.616	47.8	54.7	61.0	
	2.610	2.663	49.2	54.1	61.0	
	2.656	2.710	49.0	55.3	61.0	
	2.684	2.739	47.5	57.7	61.0	
	2.830	2.888	51.5	56.1	61.0	
	2.646	2.700	48.4	55.8	61.0	
			n = 6			
			mean	55.6		91.2
			std dev	1.2		
			CV_2	0.022		
2S	5.77	5.89	50.5	116.6	120.5	
	5.22	5.33	49.0	108.8	120.5	
	5.61	5.72	50.1	114.2	120.5	
	5.35	5.46	49.9	109.4	120.5	
	5.60	5.71	49.9	114.4	120.5	
	5.55	5.66	49.7	113.9	120.5	
			n = 6			
			mean	112.9		93.7
			std dev	3.1		
$\overline{CV}_2$	0.025		CV_2	0.027		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, 2-Butoxy Ethanol, No. S76, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Propylene Oxide, No. S75
OSHA Standard:	240 mg/cu m
Chemical used for validation:	Propylene Oxide, Lot 325604 J.T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of propylene oxide in air is described in NIOSH Method S75, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid propylene oxide to represent 5 liter air samples. Samples of propylene oxide in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of propylene oxide in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 27 minutes). The "true" value for the concentration of propylene oxide generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

This method worked satisfactorily for propylene oxide. The only major modification made was in the preparation of the charcoal tubes for desorption efficiency tests. A hexane solution of propylene oxide containing 300 mg/ml was used to apply the analyte to the charcoal. This was done so it would not be necessary to inject less than 2 microliters at the 0.5X level.

Generation

Samples of propylene oxide in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 0.0509 liter per minute, measured at 24°C, was bubbled through the propylene oxide in the generator flask, which was maintained at a temperature of 24°C. After passing through the condenser, which was maintained at 20°C, the propylene oxide vapor was diluted to the 2X level with air added at a rate of 212.8 liters per minute, measured at 24°C. Two further dilutions were made to obtain concentrations at the 1X and 0.5X level.

A Beckman Model 402 total hydrocarbon analyzer was used as a means of monitoring the generated vapor concentrations. To establish the concentrations being generated, a bag standard at 2X the OSHA standard was prepared. Once the instrument and recorder were zeroed on the dilution air, the bag concentration was monitored, and the instrument response was recorded over a period of approximately 5 minutes. Once a constant concentration level was established at 2X the OSHA standard, sampling was started by activating the sampling pumps for the 2X, 1X, and 0.5X chambers, each connected to a set of six sampling tubes. During sample collection, the generated 2X OSHA standard level was monitored continuously with the total hydrocarbon analyzer. By comparing the instrument responses for the 2X level and the bag standard, the true generated 2X concentration was established. Known dilution factors were applied to obtain the true generated concentrations at the 1X and 0.5X OSHA standard levels.

Samples were collected for 27 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 45 minutes when a concentration of 484 mg/cu m was sampled at a rate of 0.185 liter per minute.

Discussion

Two sets of desorption efficiency tests were done. In the first set preparation of the charcoal tubes for desorption efficiency tests was not done the same at each level. Hexane was used only at the 0.5X OSHA standard level in applying the propylene oxide onto the charcoal. The 1X and 2X levels were done neat. The desorption efficiency results are given below:

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.665	0.585	0.880	1.264	1.259	0.996	2.410	2.306	0.957
0.665	0.577	0.868	1.264	1.201	0.950	2.410	2.278	0.945
0.665	0.600	0.902	1.264	1.184	0.937	2.410	2.365	0.981
0.665	0.579	0.871	1.264	1.240	0.981	2.410	2.369	0.983
0.665	0.601	0.904	1.264	1.258	0.995	2.410	2.321	0.963
0.665	0.574	0.863	1.264	1.169	0.925	2.410	2.371	0.984
n=		6			6			6
mean		0.881			0.964			0.969
std dev		0.018			0.031			0.016

At the 0.5X OSHA standard level, a hexane solution of propylene oxide containing 332 mg/ml was used to apply the analyte onto the charcoal.

Desorption efficiencies were redone at all three levels (0.5X, 1X, and 2X the OSHA standard) using hexane to apply the analyte onto the charcoal. This was done to test whether spiking with hexane at all three levels or spiking with hexane at only the 0.5X level had any effect on the desorption efficiencies. The second set of desorption efficiencies did not show any significant change from the first set of desorption efficiencies. The results of the second set of desorption efficiencies are given at the end of this report, and these results were used for the statistical calculations.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for propylene oxide (Reference No. 4). The following equation was used:

$$\text{Chi Squared} = \frac{f \ln s^2 - \sum_{i=1}^{n} f_i \ln s_i^2}{1 + \frac{1}{3(n-1)} \left[\left(\sum_{i=1}^{n} \frac{1}{f_i} \right) - \frac{1}{f} \right]}$$,with n-1 degrees of freedom

where:

n = number of levels

s_i^2 = sample CV^2 of the i^{th} level

f_i = degrees of freedom associated with s_i^2 (number of samples at the i^{th} level minus one)

$i = 1, 2, 3 \ldots . n$

$$s^2 = \frac{\sum_{i=1}^{n} f_i s_i^2}{f}$$

$$f = \sum_{i=1}^{n} f_i$$

In order to pass Bartlett's test at the 1% confidence level, chi squared must be less than or equal to 9.21 when n = 3.

The sampling and analysis data gave a chi squared value of 12.0, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for propylene oxide show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.029$ $\overline{CV}_2 = 0.068$ $\overline{CV}_T = 0.085$

The average recovery at the OSHA standard level was 94.4%.

Data Sheet: Propylene Oxide S75

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.600	0.527	0.878	1.200	1.124	0.937	2.400	2.248	0.937
0.600	0.519	0.865	1.200	1.111	0.926	2.400	2.201	0.917
0.600	0.515	0.858	1.200	1.087	0.906	2.400	2.203	0.918
0.600	0.551	0.918	1.200	1.172	0.977	2.400	2.361	0.984
0.600	0.502	0.837	1.200	1.115	0.929	2.400	2.324	0.968
0.600	0.526	0.877	1.200	1.121	0.934	2.400	2.330	0.971
n =		6			6			6
mean		0.872			0.935			0.949
std dev		0.027			0.023			0.029
CV_1		0.031			0.025			0.031

$\overline{CV}_1$ 0.029

$\overline{CV}_{A+\overline{DE}}$ 0.031

Hexane was used at all 3 levels to apply the analyte onto the the charcoal for desorption efficiency experiments. A curve of desorption efficiency versus mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Propylene Oxide S75

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.437	0.517	5.22	99.0	121.0	
	0.520	0.598	5.49	108.9	121.0	
	0.515	0.593	5.68	104.4	121.0	
	0.601	0.678	5.41	125.3	121.0	
	0.567	0.644	5.25	122.7	121.0	
	0.590	0.667	5.14	129.8	121.0	
			n = 6			
			mean	115.0		95.0
			std dev	12.6		
			CV_2	0.110		
1S	0.928	1.003	4.62	217.1	241.0	
	1.037	1.115	4.78	233.3	241.0	
	1.030	1.108	4.78	231.8	241.0	
	0.977	1.054	4.54	232.2	241.0	
	0.840	0.916	4.21	217.6	241.0	
	0.969	1.046	4.48	233.5	241.0	
			n = 6			
			mean	227.6		94.4
			std dev	8.0		
			CV_2	0.035		
2S	2.422	2.552	5.08	502	482	
	2.419	2.549	5.14	496	482	
	2.374	2.502	5.05	495	482	
	2.303	2.427	4.97	488	482	
	2.264	2.386	5.05	472	482	
	2.368	2.495	5.05	494	482	
			n = 6			
			mean	491		101.9
$\overline{CV}_2$	0.068		std dev	10		
			CV_2	0.022		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Handbook for Hewlett Packard HP-65, Stat Pac 1, pp 72-73, June, 1974.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	2-Butoxy Ethanol, No. S76
OSHA Standard:	240 mg/cu m
Chemical used for validation:	2-Butoxy Ethanol, Lot 040247 Aldrich Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 2-butoxy ethanol in air is described in NIOSH Method S76, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid 2-butoxy ethanol to represent 10 liter air samples. Samples of 2-butoxy ethanol in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh Pa. The 2-butoxy ethanol was desorbed with 5% methanol in methylene chloride rather than carbon disulfide. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The concentration of 2-butoxy ethanol in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 54.6 minutes). The "true" value for the concentration of 2-butoxy ethanol generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There was only one major modification to P&CAM 127 which was to use 5% methanol in methylene chloride as the desorbing solvent instead of carbon disulfide. (See Discussion Section).

Generation

The system for generating and collecting samples of vapor from volatile liquids consists basically of a sample generator, a mixing and dilution section, and three sampling chambers. Samples are generated at a concentration 2X the OSHA standard, serial dilutions are made to 1X and 0.5X the standard, and samples are collected simultaneously at the three concentrations.

The vapor generator was adapted from the apparatus described in Reference No. 2, which has been used to measure the vapor pressure of liquids. A schematic diagram of this vapor generator is shown in Figure 1. It consists of a Pyrex glass tube which is 2.2 cm in diameter and 22.6 cm high. A coarse glass frit is sealed

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in the bottom of the tube. The bottom of the large tube is connected to a smaller tube, which is bent 180° and extends up until it is nearly as high as the large tube. The sample, which may be either a liquid or a low-melting solid, is introduced into the large tube. The apparatus is immersed in a thermostated bath with the liquid level below the bath level. Nitrogen gas flows through the small tube and passes through the frit. The small bubbles, which form at the frit, rise through the liquid and become saturated or nearly saturated with the vapor of the liquid. The bath temperature and the flow of nitrogen determine the actual amount of vapor generated. Increasing either the nitrogen flow or the bath temperature, increases the amount of vapor generated. The dilution air is introduced about 15 cm above the glass frit and just above the level of the bath. The diameter of the vapor saturation chamber is 2.2 cm. A 7 mm tube is attached to the inner wall about 8.5 cm above the frit. The 7 mm tube extends about 2.2 cm into another section of 2.2 cm diameter tubing. The dilution air is admitted by another tube located between the top and bottom of the 7 mm tube. Sufficient dilution air is added to dilute the vapor in nitrogen to the desired concentration, which is usually twice the OSHA standard. Vapor saturation of the air stream with the analyte must not be exceeded to produce a well-mixed stream of the analyte in air.* The generation conditions used for 2-butoxy ethanol to generate a concentration twice the OSHA standard (490 mg/cu m) are given in Table 1.

Table 1

Generator Conditions for 2-Butoxy Ethanol

Nitrogen flow rate (liter/minute)	2.32
Dilution air flow rate (liter/minute)	34.7
Bath temperature (°C)	31

The equations given in Reference No. 2 can be used to calculate the vapor concentration in the saturated nitrogen stream. Since there is no assurance that the nitrogen is exactly 100% saturated and since in many cases the vapor pressure at the bath temperature is not known accurately, these equations were not used. The concentration of analyte in each chamber in the generator was measured using a Beckman Model 402 total hydrocarbon analyzer. The analyzer was calibrated using bag standards as described in Reference No. 1.

Two sets of matched orifices are used to pull the vapors into the sampling chambers and to make the necessary secondary dilutions so that the concentrations in the three chambers are at 2X, 1X, and 0.5X the OSHA standard.

*If the vapor saturation concentration is exceeded then particles of the analyte will be formed in the cool air stream.

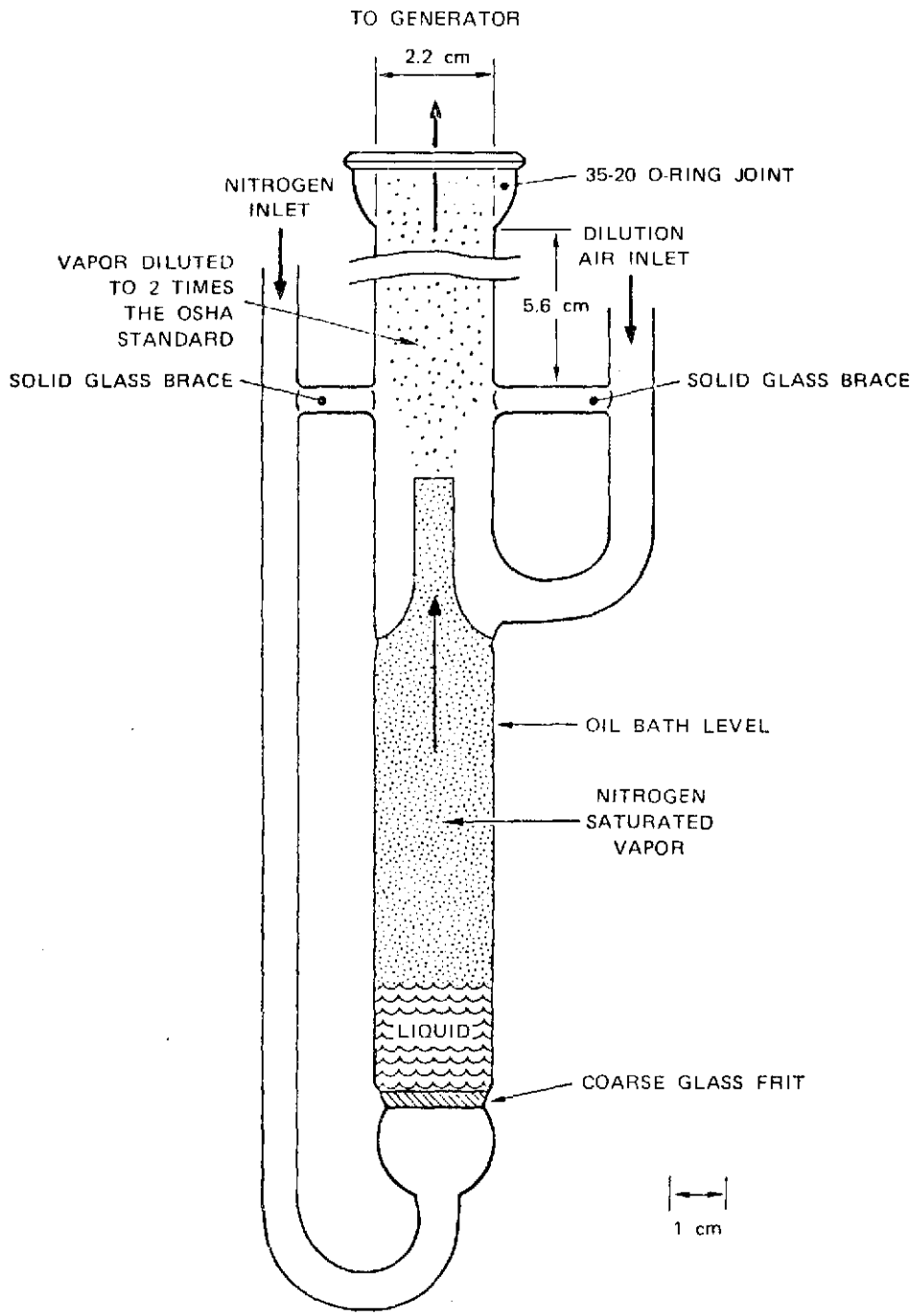

FIGURE 1 VAPOR GENERATOR

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After primary dilution, the vapor at 2X the standard concentration enters a stainless steel transfer line, the other end of which is connected to a pump through a critical orifice. The three sampling chambers branch off this line. The generated vapor is split at the first sampling chamber by a pump connected through a critical orifice to the bottom of the first chamber. This chamber now contains an atmosphere at 2X the standard as generated. Diluting air enters the transfer line immediately following the branch-off to the first chamber, mixes with the vapor sample, and the vapor at the new concentration of 1X the standard is again split by pumping into the second chamber. Another dilution is made in the transfer line following the second chamber, to obtain the concentration needed for the 0.5X level. A pump connected to the bottom of the third sampling chamber pulls sample at this concentration into this chamber.

The two sets of orifices used to obtain these dilutions have been chosen so that the desired directions of flow are maintained in the system, and so the appropriate dilutions are made between the first and second, and second and third chambers. The orifices connected to the outlet of the transfer line and to the three sampling chambers operate at 13.5 liters per minute. The pressure of the secondary dilution air entering the line between the chambers is set so that each orifice admits air at a flow of 13.5 liters per minute. On the basis of the orifice calibrations, the concentration in the 1X chamber is 0.500 times the concentration in the 2X chamber and the concentration in the 0.5X chamber is 0.250 times the concentration in the 2X chamber.

The three sampling chambers are identical. Each consists of a stainless steel cone, the top of which is connected to the transfer line, and the bottom of which is fitted to a cylindrical section. The base of the cylindrical section contains the fittings necessary to hold six samples in a vertical position, plus a centered outlet to the pump mentioned above. The six sample ports are connected through six matching critical orifices to a sampling pump. A separate metal bellows vacuum pump is used for sampling each chamber.

Generation of vapors at the desired concentration is accomplished by adjusting the flows of nitrogen gas through the generating flask and of the primary dilution air. Adjustments for further dilutions to the 1X and 0.5X levels are not necessary since this secondary dilution is controlled automatically by the system of orifices described above.

Samples of 2-butoxy ethanol were collected for 54.6 minutes at a rate of 0.185 liter per minute.

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene. (Reference No. 1). Less than 5% of the generated concentration of 480 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.183 liter per minute, indicating a capacity of at least 21 mg of 2-butoxy ethanol in the charcoal tube.

Discussion

It was necessary to find another eluent for the method, because carbon disulfide gave a poor recovery at 1X the OSHA standard level. Several solvents were tried, and the results are given in the table below.

Desorption Efficiency Trials

Solvent (0.5 ml each)	mg Taken	mg Found	D.E.
Carbon disulfide	2.437	1.465	0.601
Carbon disulfide with 5% methanol	2.437	1.760	0.722
Methylene chloride	2.437	2.093	0.859
Methylene chloride with 5% methanol	2.437	2.369	0.972

From the above experiments 5% methanol in methylene chloride was selected as the eluent for the method.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.009$ $\overline{CV}_2 = 0.033$ $\overline{CV}_T = 0.060$

The average recovery at the OSHA standard level was 92%.

Data Sheet: 2-Butoxy Ethanol S76

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.264	1.215	0.961	2.437	2.395	0.983	4.87	4.80	0.986
1.264	1.243	0.983	2.437	2.404	0.986	4.87	4.75	0.975
1.264	1.268	1.003	2.437	2.428	0.996	4.87	4.80	0.986
1.264	1.255	0.993	2.437	2.404	0.986	4.87	4.77	0.979
1.264	1.263	0.999	2.437	2.403	0.986	4.87	4.78	0.982
1.264	1.252	0.990	2.437	2.409	0.988	4.87	4.80	0.986

n=	6	6	6
mean	0.988	0.988	0.982
std dev	0.015	0.004	0.005
CV_1	0.015	0.004	0.005

$\overline{CV}_1$ 0.009

$\overline{CV}_{A+\overline{DE}}$ 0.010

A desorption efficiency of 0.986 was used for calculation of the corrected mg in the Sampling and Analysis table at all three levels.

Data Sheet: 2-Butoxy Ethanol S76

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	1.276	1.294	11.37	113.8	124.4	
	1.206	1.223	10.49	116.6	124.4	
	1.172	1.189	10.27	115.8	124.4	
	1.252	1.270	10.82	117.4	124.4	
	1.150	1.166	10.44	111.7	124.4	
	1.246	1.264	10.98	115.1	124.4	
			n = 6			
			mean	115.1		92.5
			std dev	2.1		
			CV_2	0.018		
1S	2.244	2.276	9.56	238.1	248.0	
	1.696	1.720	8.42	204.3	248.0	
	2.120	2.150	9.24	232.7	248.0	
	2.184	2.215	9.56	231.7	248.0	
	2.034	2.063	8.96	230.2	248.0	
	2.072	2.101	9.07	231.6	248.0	
			n = 6			
			mean	228.1		92.0
			std dev	12.0		
			CV_2	0.053		
2S	4.95	5.02	10.27	489	490	
	4.46	4.52	9.67	467	490	
	4.77	4.84	10.16	476	490	
	4.73	4.80	10.11	475	490	
	4.74	4.81	10.11	476	490	
	4.70	4.77	9.95	479	490	
			n = 6			
			mean	477		97.3
			std dev	7		
$\overline{CV}_2$	0.033		CV_2	0.015		

* All values have pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Physical Methods of Chemistry, Part V, A. Weissberger and B.W. Rossiter, eds. John Wiley & Sons, 1971, pp.61-66.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Isopropyl Glycidyl Ether, No. S77
OSHA Standard:	240 mg/cu m
Chemical used for validation:	Isopropyl Glycidyl Ether, Lot 681-X Eastman Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of isopropyl glycidyl ether in air is described in NIOSH Method S77, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid isopropyl glycidyl ether to represent 10 liter air samples. Samples of isopropyl glycidyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of isopropyl glycidyl ether in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 55 minutes). The "true" value for the concentration of isopropyl glycidyl ether generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of isopropyl glycidyl ether in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 706 ml/minute was bubbled through the isopropyl glycidyl ether in the generator flask, which was maintained at 35°C. After passing through the condenser, which was water cooled to 19.7°C, the isopropyl glycidyl ether was diluted to the 2X level with air added at a rate of 42.5 liters per minute. Two further dilutions were made to obtain concentrations at the 1X and 0.5X levels.

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 2). The three sampling chambers were monitored alternately during the time samples were being collected. Samples were collected for 55 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Less than 5% of the generated concentration of 480 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.183 liter per minute, indicating a capacity of at least 21 mg of isopropyl glycidyl ether in the charcoal tube.

Discussion

The first set of generated samples had two low results at the 0.5X level. A second test was therefore conducted to obtain a set of six samples at the 0.5X level. The data for the first set, which were not used in the calculation of precision and accuracy, are as follows:

Concentration		Remarks
Taken (mg/cu m)	Found (mg/cu m)	
123	109.5	
123	107.4	
123	109.3	
123	105.0	
123	60.1	Leaky orifice
123	70.2	Sample loss during analysis

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.020$ $\overline{CV}_2 = 0.044$ $\overline{CV}_T = 0.067$

The average recovery at the OSHA standard level was 93%.

Data Sheet: Isopropyl Glycidyl Ether, S77

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.195	0.930	0.778	2.389	2.016	0.844	4.78	4.45	0.931
1.195	0.927	0.776	2.389	1.932	0.809	4.78	4.47	0.935
1.195	0.964	0.807	2.389	2.004	0.839	4.78	4.46	0.933
1.195	0.938	0.785	2.389	2.003	0.838	4.78	4.38	0.916
1.195	0.884	0.740	2.389	1.988	0.832	4.78	4.40	0.921
1.195	0.914	0.765	2.389	2.009	0.841	4.78	4.33	0.906
n=		6			6			6
mean		0.775			0.834			0.924
std dev		0.022			0.013			0.011
CV_1		0.028			0.016			0.012

$\overline{CV}_1$ 0.020

$\overline{CV}_{A+\overline{DE}}$ 0.022

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Isopropyl Glycidyl Ether, S77

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.929	1.199	10.26	116.9	121.3	
	0.848	1.101	9.94	110.8	121.3	
	0.839	1.091	10.10	108.0	121.3	
	0.888	1.149	10.16	113.1	121.3	
	0.911	1.177	9.99	117.8	121.3	
	0.885	1.146	10.10	113.5	121.3	
			n = 6			
			mean	113.4		93.5
			std dev	3.7		
			CV_2	0.033		
1S	1.452	1.799	8.41	213.9	243.1	
	1.771	2.149	9.23	232.8	243.1	
	1.656	2.024	8.95	226.2	243.1	
	1.780	2.160	9.56	225.9	243.1	
	1.781	2.161	9.56	226.0	243.1	
	1.730	2.105	9.06	232.3	243.1	
			n = 6			
			mean	226.2		93.0
			std dev	6.8		
			CV_2	0.030		
2S	4.36	4.73	10.10	468	484	
	4.63	4.98	10.26	485	484	
	4.20	4.58	9.94	461	484	
	4.44	4.81	10.10	476	484	
	3.64	4.04	9.99	404	484	
	4.38	4.75	10.16	468	484	
			n = 6			
			mean	460		95.0
			std dev	29		
$\overline{CV}_2$	0.044		CV_2	0.063		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Tetrahydrofuran, No. S78
OSHA Standard:	590 mg/cu m
Chemical used for validation:	Tetrahydrofuran, Lot XAH Mallinckrodt Analytical Reagent

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of tetrahydrofuran in air is described in NIOSH Method S78, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid tetrahydrofuran to represent 9 liter air samples. Samples of tetrahydrofuran in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of tetrahydrofuran in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 48 minutes). The "true" value for the concentration of tetrahydrofuran generated was determined by comparison with a "bag" standard using a hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of tetrahydrofuran in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 102 ml/minute measured at 22.5°C, was bubbled through the tetrahydrofuran in the generator flask, which was maintained at a temperature of 45°C. After passing through the condenser, which was water cooled to 20°C, the tetrahydrofuran vapor was diluted to the 2X level with air added at a rate of 64.9 liters per minute measured at 22.5°C. Two further dilutions were made to obtain concentrations at the 1X and 0.5X levels.

Samples were collected for 48 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate.

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Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene. (Reference No. 2). Breakthrough occurred in 72 minutes when a concentration of 1140 mg/cu m was sampled at a rate of 0.185 liter per minute.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.016$ $\overline{CV}_2 = 0.021$ $\overline{CV}_T = 0.055$

The average recovery at the OSHA standard level was 98.6%.

Data Sheet: Tetrahydrofuran S78

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
3.00	2.679	0.893	5.92	5.68	0.959	11.83	11.16	0.943
3.00	2.737	0.912	5.92	5.67	0.958	11.83	11.26	0.952
3.00	2.744	0.915	5.92	5.67	0.958	11.83	11.10	0.938
3.00	2.761	0.920	5.92	5.62	0.949	11.83	11.06	0.935
3.00	2.668	0.889	5.92	5.45	0.921	11.83	11.17	0.944
3.00	2.735	0.912	5.92	5.47	0.924	11.83	11.46	0.969
n=		6			6			6
mean		0.907			0.945			0.947
std dev		0.013			0.018			0.012
CV_1		0.014			0.019			0.013

$\overline{CV}_1$ 0.016

$\overline{CV}_{A+\overline{DE}}$ 0.017

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Tetrahydrofuran S78

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	2.550	2.793	8.99	311	323	
	2.704	2.946	9.61	307	323	
	2.612	2.855	9.18	311	323	
	2.807	3.058	9.94	308	323	
	2.608	2.850	9.13	312	323	
	2.861	3.110	9.46	329	323	
			n = 6			
			mean	313		96.9
			std dev	8		
			CV_2	0.026		
1S	5.08	5.39	8.37	644	636	
	4.97	5.27	8.37	630	636	
	4.72	5.02	7.93	633	636	
	4.69	4.99	7.84	636	636	
	4.60	4.89	8.08	605	636	
	4.25	4.53	7.36	615	636	
			n = 6			
			mean	627		98.6
			std dev	14		
			CV_2	0.022		
2S	9.57	10.09	8.70	1160	1240	
	9.69	10.22	8.99	1137	1240	
	9.74	10.27	8.84	1162	1240	
	9.64	10.17	8.84	1150	1240	
	9.75	10.28	8.89	1156	1240	
	9.51	10.03	8.84	1135	1240	
			n = 6			
			mean	1150		92.7
$\overline{CV}_2$	0.021		std dev	12		
			CV_2	0.010		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Methyl Cellosolve, No. S79
OSHA Standard:	80 mg/cu m
Chemical used for validation:	Methyl Cellosolve, Lot 041647 Aldrich Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of methyl cellosolve in air is described in NIOSH Method S79, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid methyl cellosolve to represent 50 liter air samples. Samples of methyl cellosolve in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The methyl cellosolve was desorbed with 5% methanol in methylene chloride rather than carbon disulfide. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The concentration of methyl cellosolve in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 53.5 minutes). The "true" value for the concentration of methyl cellosolve generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There was only one major modification to P&CAM 127 which was to use 5% methanol in methylene chloride as the eluent rather than carbon disulfide. (See Discussion Section)

Generation

Samples of methyl cellosolve in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Two sets of samples were generated (See Discussion Section). Data for the 2X and 1X OSHA standard levels were used from one set; the 0.5X OSHA standard level data was used from a second set. The 2X and 1X samples were generated using a flow of nitrogen through the generator of 246 ml/minute. This was diluted to the 2X OSHA level by addition of air at a rate of 43.5 liters per minute, and further diluted to the 1X OSHA level. For the set of samples from

which the 0.5X OSHA level was analyzed, nitrogen flow was 250 ml per minute through the generator, and dilution air was added at a rate of 40.6 liters per minute to the 2X concentration, which was then diluted to obtain the 0.5X concentration. In both tests the methyl cellosolve was held at 116°C in the generator flask. The vapors carried out of the flask by nitrogen were passed through a condenser maintained at 20°C before dilution with air.

A Beckman Model 402 total hydrocarbon analyzer was used to alternately monitor the concentration of vapors at all three levels in the sampling chambers during collection of samples (Reference No. 2). Samples were collected for 53.5 minutes at a rate of approximately 1 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 138 minutes when a concentration of 158 mg/cu m was sampled at a rate of 0.93 liter per minute.

Discussion

It was necessary to find another eluent for the method, because carbon disulfide gave poor recoveries at 0.5X, 1X, and 2X the OSHA standard levels. Several solvents were tried, and the results are given in the table below:

Desorption Efficiency Trials

Solvent (0.5 ml each)	mg Taken	mg Found	D.E.
Carbon disulfide	2.03	0.789	0.389
	4.05	2.14	0.528
	4.05	2.25	0.555
	8.11	5.18	0.639
Carbon disulfide with 5% methanol	4.05	1.72	0.425
Methylene chloride	4.05	3.52	0.869
Methylene chloride with 5% methanol	4.05	3.88	0.958

From the above experiments it was decided to use 5% methanol in methylene chloride as the eluent for the method.

It was necessary to generate two sets of samples. The 0.5X data set is taken from the first test; the 1X and 2X data sets are taken from the second test.

The second test was necessary because two samples at the 2X OSHA level of the first set gave low results when analyzed. No material was found on the backup sections of the low sample tubes. The second set of generated samples also had one low result at 2X level. These results were low due to improperly operating flow orifices. The "found" values for the 2X OSHA level of the first test were:

mg/cu m found
163
160
161
164
117
96

These figures are for information only, as they were not used in the calculations for precision and accuracy.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for methyl cellosolve as in Reference No. 4.

The sampling and analysis data gave a chi squared value of 14.7, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for methyl cellosolve show excellent precision. Therefore pooling will not introduce significant error. For this reason CV_T is calculated on all the data.

Grubbs' test for outliers was calculated at each level as follows:

$$G_o = \left| \frac{x_o - \bar{x}}{s} \right|$$

where x_o is the smallest (or greatest) value for the found concentrations at the level of interest, and where, for n samples,

$$\bar{x} = 1/n \sum_{i=1}^{n} x_i$$

$$s = \sqrt{\frac{n-1}{n}} \text{ X std. dev.}$$

For example, using the smallest value of x_i for methyl cellosolve at the 1X OSHA standard level,

$$G_o = \left|\frac{65.0 - 75.6}{5.02}\right| = 2.11$$

For the largest value of x_i,

$$G_o = \left|\frac{81.0 - 75.6}{5.02}\right| = 1.08$$

In order to pass Grubbs' test at the 1% confidence level, G_o must be equal to or be less than 2.13 (Reference No. 5). If G_o is greater than 2.13, the number in question is an outlier. Since $x_o = 65$ and $x_o = 81$ gave G_o's that were less than 2.13, these values are not considered outliers.

The statistical procedures used are described in Reference No. 3.

$$\overline{CV}_1 = 0.008 \qquad \overline{CV}_2 = 0.046 \qquad \overline{CV}_T = 0.068$$

The average recovery at the OSHA standard level was 92.8%.

Data Sheet: Methyl Cellosolve S79

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
2.027	1.980	0.977	4.05	3.90	0.963	8.11	7.98	0.984
2.027	1.948	0.961	4.05	4.02	0.993	8.11	7.97	0.983
2.027	1.966	0.970	4.05	3.97	0.980	8.11	7.88	0.972
2.027	1.939	0.957	4.05	3.98	0.983	8.11	8.02	0.989
2.027	1.937	0.956	4.05	4.00	0.988	8.11	7.95	0.980
2.027	1.962	0.968	4.05	3.95	0.975	8.11	7.98	0.984
n=		6			6			6
mean		0.965			0.980			0.982
std dev		0.008			0.010			0.006
CV_1		0.008			0.010			0.006

$\overline{CV}_1$ 0.008

$\overline{CV}_{A+\overline{DE}}$ 0.009

A desorption efficiency of 0.976 was used for calculation of the corrected mg in the Sampling and Analysis table at all three levels.

Data Sheet: Methyl Cellosolve S79

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	2.042	2.092	50.5	41.4	43.7	
	2.128	2.180	52.0	41.9	43.7	
	2.155	2.208	52.1	42.4	43.7	
	2.124	2.176	51.5	42.3	43.7	
	2.124	2.176	51.4	42.3	43.7	
	2.119	2.171	51.8	41.9	43.7	
			n = 6			
			mean	42.0		96.2
			std dev	0.4		
			CV_2	0.010		
1S	3.67	3.76	49.0	76.7	81.5	
	3.61	3.70	48.4	76.4	81.5	
	3.78	3.87	47.8	81.0	81.5	
	3.75	3.84	49.3	77.9	81.5	
	3.67	3.76	49.0	76.7	81.5	
	3.02	3.09	47.5	65.0	81.5	
			n = 6			
			mean	75.6		92.8
			std dev	5.5		
			CV_2	0.073		
2S	7.44	7.62	49.9	152.7	160.0	
	7.54	7.73	49.7	155.5	160.0	
	7.81	8.00	50.1	159.7	160.0	
	7.52	7.70	49.9	154.3	160.0	
	7.32	7.50	50.5	148.5	160.0	
	(Sample not acceptable - leaky orifice).					
			n = 5			
			mean	154.1		96.3
			std dev	4.1		
$\overline{CV}_2$ 0.046			CV_2	0.027		

* All values have passed the Grubbs' outlier test at the 1% confidence level as explained under Precision and Accuracy.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

5. Sarban, A.E. & Greenburg, B., Contributions to Order Statistics, John Wiley, 1962, pp. 302-303.

Backup Data Report

Substance:	Ethyl Ether, No S80
OSHA Standard:	1210 mg/cu m
Chemical used for validation:	Ethyl Ether, Lot BLL Mallinckrodt Analytical Reagent

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of ethyl ether in air is described in NIOSH Method S80, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid ethyl ether to represent 3 liter air samples. Samples of ethyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The ethyl ether was desorbed with ethyl acetate rather than carbon disulfide. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The concentration of ethyl ether in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 16 minutes). The "true" value for the concentration of ethyl ether generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There was only one major modification made to P&CAM 127, which was to use ethyl acetate as the desorbing solvent rather than carbon disulfide. (See Discussion)

Generation

Samples of ethyl ether in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 0.162 liter per minute was bubbled through the ethyl ether in the generator flask, which was maintained at a temperature of 24°C. After passing through the condenser, which was water cooled to 20°C, the ethyl ether vapor was diluted to the 2X OSHA standard level with air added at a rate of 257 liters per minute. Two further dilutions were made to obtain concentrations at the 1X and 0.5X OSHA standard levels.

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 2). The three sampling chambers were monitored alternately during the time the samples were being collected. Samples were collected for 16 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 33 minutes when a concentration of 2470 mg/cu m was sampled at a rate of 0.185 liter per minute.

Discussion

It was necessary to choose another eluent for the method, because carbon disulfide gave a peak that interfered with the ethyl ether peak on the gas chromatogram. The GC conditions were as follows:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 195°C injector temperature
5. 250°C manifold temperature
6. 175°C column temperature

The gas chromatographic column consisted of a 4-ft long by 1/4-in O.D. stainless steel tube packed with 50/80 mesh Porapak Q. A glass tube containing Porapak Q was tested, but this column did not give any improvement.

Several solvents were tested as described below:

1. 3.54 mg of ethyl ether in 0.5 ml carbon disulfide was tested. The carbon disulfide peak was found to interfere with the ethyl ether peak.

2. 3.54 mg of ethyl ether in 0.5 ml hexane was tested. The hexane peak was also found to interfere with the ethyl ether peak.

3. 3.54 mg of ethyl ether in 0.5 ml 2-butanone was tested, and 2-butanone was found to interfere with the ethyl ether peak.

4. 3.54 mg of ethyl ether in 0.5 ml ethyl acetate was tested. The resulting ethyl ether peak was nicely shaped, and the ethyl acetate peak did not interfere.

From the above experiments, it was decided to use ethyl acetate as the eluent for this method.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.024$ $\overline{CV}_2 = 0.014$ $\overline{CV}_T = 0.053$

The average recovery at the OSHA standard level was 105.1%.

Data Sheet: Ethyl Ether S80

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.770	1.776	1.003	3.54	3.55	1.003	7.08	6.79	0.959
1.770	1.684	0.951	3.54	3.53	0.997	7.08	6.94	0.980
1.770	1.759	0.994	3.54	3.48	0.983	7.08	6.87	0.970
1.770	1.628	0.920	3.54	3.52	0.994	7.08	7.08	1.000
1.770	1.658	0.937	3.54	3.61	1.020	7.08	7.13	1.007
1.770	1.748	0.988	3.54	3.56	1.007	7.08	6.92	0.977
n=		6			6			6
mean		0.966			1.001			0.982
std dev		0.034			0.013			0.018
CV_1		0.035			0.013			0.018

$\overline{CV}_1$ 0.024

$\overline{CV}_{A+\overline{DE}}$ 0.026

A desorption efficiency of 0.983 was used for calculation of the corrected mg in the Sampling and Analysis table at all three levels.

Data Sheet: Ethyl Ether S80

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	1.902	1.935	3.08	628	606	
	2.128	2.165	3.41	635	606	
	1.975	2.009	3.13	642	606	
	2.040	2.075	3.25	638	606	
	1.964	1.998	3.15	634	606	
	2.044	2.079	3.30	630	606	
			n = 6			
			mean	634		104.7
			std dev	5		
			CV_2	0.008		
1S	3.01	3.06	2.53	1209	1195	
	3.58	3.64	2.87	1268	1195	
	3.48	3.54	2.77	1278	1195	
	3.31	3.37	2.72	1239	1195	
	3.33	3.39	2.69	1260	1195	
	3.61	3.67	2.87	1279	1195	
			n = 6			
			mean	1256		105.1
			std dev	27		
			CV_2	0.021		
2S	7.58	7.71	3.03	2544	2400	
	7.34	7.47	2.98	2507	2400	
	7.56	7.69	3.03	2538	2400	
	7.80	7.93	3.08	2575	2400	
	7.46	7.59	3.03	2505	2400	
	7.60	7.73	3.05	2534	2400	
			n = 6			
			mean	2534		105.6
			std dev	26		
$\overline{CV}_2$	0.014		CV_2	0.010		

*All values passed Grubbs' outlier test at the 1% confidence level, as described in Reference No. 4.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: n-Butyl Glycidyl Ether, No. S81

OSHA Standard: 270 mg/cu m

Chemical used for validation: n-Butyl Glycidyl Ether
Electron Microscopy Sciences

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of n-butyl glycidyl ether in air is described in NIOSH Method S81, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid n-butyl glycidyl ether to represent 10 liter air samples. Samples of n-butyl glycidyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.) by use of the D.E. curve. The concentration of n-butyl glycidyl ether in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54 minutes). The "true" value for the concentration of n-butyl glycidyl ether generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 2.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of n-butyl glycidyl ether in air at the 2X and 1X levels were generated using the vapor generator method described in the Backup Data Report for cumene (Reference No. 1). The samples at the 0.5X level were generated using the syringe injection technique described in the Backup Data Report for Phenyl Ether-Biphenyl Mixture (Reference No. 3). The reason for generating two sets of samples is given in the Discussion section below.

Conditions for the two tests were as follows:

Vapor Generator: Approximately 25 ml of the analyte was contained in a 500-ml round bottom flask at 110°C. Nitrogen gas at a flow rate of 2.164 liters per minute was bubbled through

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the heated liquid, and carried vapors out the flask through a 20°C-condenser. The exiting stream of vapors was diluted to the 2X level with air at a rate of 31 liters per minute. A further dilution was made to obtain the 1X level. For details of this generator and dilution system, see Reference No. 1.

Syringe Injection: This technique is described fully in Reference No. 3. The syringe drive was set to deliver a constant amount of analyte (nominally 19.1 microliters/minute by manufacturer's specifications) into a heated inlet system, through which nitrogen was flowing at a rate of 1.161 liters per minute. These vapors were diluted with air at a rate of 129 liters per minute to obtain the 0.5X concentration.

For both tests bag standards were used to determine the concentration. The sampling chambers were monitored continuously during sample collection, using a Beckman Model 402 total hydrocarbon analyzer (Reference No. 2). Samples were collected for 54 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Less than 5% of the generated concentration of 530 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.183 liter per minute, indicating a capacity of at least 23 mg of n-butyl glycidyl ether in the charcoal tube.

Discussion

Two sets of samples were generated to complete this study. Six samples at each of the three levels (2X, 1X, and 0.5X the OSHA standard) were generated and collected during the first test. Analysis of the samples at the 0.5X level indicated an average recovery of 83%. These low results could not be explained, therefore, a second set of samples at the 0.5X level were generated and collected. Data for the 0.5X level of the first set are given below. These data were not used in calculation of the precision and accuracy of the method.

	Found mg/cu m	Taken mg/cu m
	116.7	131
	106.2	131
	105.1	131
	108.2	131
	105.0	131
	109.0	131
Mean	108.4	
Recovery	83%	

The second set of samples at the 0.5X level also had a low recovery (85.1%). From these two tests it is assumed that this low recovery at the 0.5X level is characteristic of the method.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.016$ $\overline{CV}_2 = 0.054$ $\overline{CV}_T = 0.074$

The average recovery at the OSHA standard level was 98.2%.

Data Sheet: n-Butyl Glycidyl Ether S81

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.552	1.292	0.832	3.196	2.859	0.895	6.39	5.96	0.933
1.552	1.288	0.830	3.196	2.706	0.847	6.39	5.94	0.930
1.552	1.308	0.843	3.196	2.794	0.874	6.39	5.99	0.937
1.552	1.242	0.800	3.196	2.786	0.872	6.39	5.99	0.937
1.552	1.256	0.809	3.196	2.791	0.873	6.39	5.93	0.928
1.552	1.305	0.841	3.196	2.782	0.870	6.39	5.90	0.923
n=		6			6			6
mean		0.826			0.872			0.931
std dev		0.018			0.015			0.005
CV_1		0.022			0.017			0.005

$\overline{CV}_1$ 0.016

$\overline{CV}_{A+\overline{DE}}$ 0.017

A curve of desorption efficiency vs. mg found was drawn by hand. This curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: n-Butyl Glycidyl Ether S81

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m *	mg/cu m	Recovery
0.5S	0.902	1.119	9.84	113.7	133.0	
	0.955	1.182	10.00	118.2	133.0	
	0.903	1.120	10.05	111.4	133.0	
	1.029	1.267	10.16	124.7	133.0	
	0.922	1.143	10.00	114.3	133.0	
	0.771	0.967	10.00	96.7	133.0	
			n = 6			
			mean	113.2		85.1
			std dev	9.3		
			CV_2	0.082		
1S	2.073	2.430	9.56	254.2	259.0	
	2.066	2.422	9.56	253.3	259.0	
	1.941	2.286	9.07	252.0	259.0	
	1.971	2.319	8.96	258.8	259.0	
	2.088	2.448	9.24	264.9	259.0	
	1.722	2.045	8.42	242.9	259.0	
			n = 6			
			mean	254.4		98.2
			std dev	7.3		
			CV_2	0.029		
2S	4.80	5.26	10.16	518	542	
	5.07	5.53	10.11	547	542	
	5.26	5.72	10.27	557	542	
	4.99	5.45	10.11	539	542	
	4.95	5.41	9.95	544	542	
	(Sample was lost.)					
			n = 5			
			mean	541		99.8
			std dev	14		
$\overline{CV}_2$ 0.054			CV_2	0.026		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Phenyl Ether-Biphenyl Mixture, No. S73, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Cyclohexene, No. S82
OSHA Standard:	1010 mg/cu m
Chemical used for validation:	Cyclohexene, Lot #234601 J.T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of cyclohexene in air is described in NIOSH Method S82, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid cyclohexene to represent 5 liter air samples. Samples of cyclohexene in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The concentration of cyclohexene in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 27 minutes). The "true" value for the concentration of cyclohexene generated was determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described below.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of cyclohexene in air were generated by the procedure described in the Backup Data Report for cumene (Reference No. 1). Nitrogen at a rate of 0.459 liter per minute measured at 23.5°C was bubbled through the cyclohexene in the generator flask, which was maintained at a temperature of 40°C. After passing through the condenser, which was maintained at 20°C, the cyclohexene vapor was diluted to the 2X level with air added at a rate of 32.3 liters per minute measured at 23.5°C. Two further dilutions were made to obtain concentrations at the 1X and 0.5X level.

A Beckman Model 402 total hydrocarbon analyzer was used as a means of monitoring the generated vapor concentrations. To establish the concentrations being generated, a bag standard at 2X the OSHA standard was prepared. Once the instrument and recorder were zeroed on the dilution air, the bag concentration was monitored, the instrument response was recorded over a period of approximately 5 minutes. Once a constant concentration level was established at 2X the OSHA standard,

sampling was started by activating the sampling pumps for the 2X, 1X, and 0.5X chambers, each connected to a set of six sampling tubes. During sample collection, the generated 2X OSHA standard level was monitored continuously with the total hydrocarbon analyzer. By comparing the instrument responses for the 2X level and the bag standard, the true generated 2X concentration was established. Known dilution factors were applied to obtain the true generated concentrations at the 1X and 0.5X OSHA standard levels.

Breakthrough

The breakthrough time was determined at a vapor concentration equal to twice the OSHA standard level. It is defined as the time at which the effluent concentration from the first (100 mg) section of the charcoal tube reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube during collection of a field sample.

To measure the breakthrough time, 6 tubes containing the first (100 mg) section of charcoal were tested in parallel. The tubes were placed in the sample generation apparatus. The test atmosphere was pulled through each tube at an average flow of 0.185 ml/minute, using 0.006 inch diameter orifices to regulate the flow. The orifices were connected to a manifold, which was evacuated to about 22 inches Hg using a metal bellows pump. This pump was selected, because it does not leak and is constructed entirely of stainless steel; therefore, it will not alter the composition of the test atmosphere.

Measurements of the concentration of the vapor in the sample generation apparatus and the effluent from the sampling pump were made with a total hydrocarbon analyzer. Dilution air used for adjusting the concentration of vapor in the sampling chamber was also used to zero the strip chart recorder of the hydrocarbon analyzer. A "bag" standard of cyclohexene in air at a concentration of 2 times the OSHA standard was used for calibration. The magnitude of the analyzer response as indicated by the strip chart recorder for the bag standard was compared with the response for the material in the 2X chamber to determine the vapor concentration in the chamber.

After determining the concentration of cyclohexene in the 2X chamber, the outlet to the sampling pump was connected to the inlet of the hydrocarbon analyzer, and the breakthrough experiment was begun. The effluent from the pump was monitored during the period of the test, and the response of the analyzer during the test was recorded. If channeling had occurred in one or more tubes an abnormal response would have resulted. Sharp rises in effluent concentration, followed by an apparent leveling off, would have been observed early in the run.

For instance, if one tube had channeled, the effluent concentration would have risen sharply to about 17% of the concentration in the test atmosphere, but, since the flow through each tube was regulated separately, it would not have risen appreciably above 17% until breakthrough occurred in the other tubes. If channeling had occurred, it would have been necessary to repeat the experiment with a second set of tubes.

A normal breakthrough curve was obtained with breakthrough at 56 minutes, and the total volume sampled was 10 liters.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for cyclohexene as in Reference No. 3.

The sampling and analysis data gave a chi squared value of 21.2, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for cyclohexene show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.021$ $\overline{CV}_2 = 0.052$ $\overline{CV}_T = 0.073$

The average recovery at the OSHA standard level was 109%.

Data Sheet: Cyclohexene S82

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
2.430	2.471	1.017	4.85	4.89	1.008	9.72	10.11	1.040
2.430	2.375	0.977	4.85	4.93	1.016	9.72	10.01	1.030
2.430	2.457	1.011	4.85	4.93	1.016	9.72	9.91	1.020
2.430	2.409	0.991	4.85	4.95	1.021	9.72	9.29	0.956
2.430	2.454	1.010	4.85	4.98	1.027	9.72	9.89	1.017
2.430	2.511	1.033	4.85	4.89	1.008	9.72	10.09	1.038
n =		6			6			6
mean		1.006			1.016			1.017
std dev		0.020			0.007			0.031
CV_1		0.020			0.007			0.030

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{DE}}$ 0.023

A desorption efficiency of 1.013 was used for calculation of the corrected mg in the Sampling and Analysis table at all three levels.

Data Sheet: Cyclohexene S82

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m *	mg/cu m	Recovery
.05S	3.134	3.094	5.68	545	510	
	3.148	3.108	5.49	566	510	
	2.978	2.940	5.14	572	510	
	3.164	3.123	5.41	577	510	
	2.928	2.890	5.25	550	510	
	3.072	3.033	5.22	581	510	
			n = 6			
			mean	565		111
			std dev	15		
			CV_2	0.026		
1S	5.46	5.39	4.21	1280	1020	
	4.64	4.58	4.62	991	1020	
	5.14	5.07	4.78	1061	1020	
	5.35	5.28	4.78	1105	1020	
	5.09	5.02	4.54	1106	1020	
	5.21	5.14	4.48	1147	1020	
			n = 6			
			mean	1115		109
			std dev	97		
			CV_2	0.087		
2S	11.85	11.70	5.14	2276	2030	
	11.60	11.45	5.06	2263	2030	
	11.62	11.47	5.06	2267	2030	
	11.63	11.48	5.08	2260	2030	
	11.50	11.35	4.97	2284	2030	
	11.78	11.63	5.06	2298	2030	
			n = 6			
			mean	2275		112
			std dev	14		
$\overline{CV}_2$ 0.052			CV_2	0.006		

* All values have pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Naphtha, Coal Tar

OSHA Standard: 400 mg/cu m

Chemical used for validation: 2-50-W Hi-Flash® Solvent, Neville Chemical Co. (Boiling range: 154-195°C ; density: 0.893 g/ml)

Procedure

The general procedure used is described in NIOSH Method No. S86 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of coal tar naphtha represented in a 10-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 -ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. Coal tar naphtha is a mixture of hydrocarbons and all data are based on integrating the total area of relevant peaks. Desorption efficiencies were determined by plotting the DE values obtained for the 0.5X, 1X and 2X the OSHA standard and hand-drawing the best-fit curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 was used but the calibration technique was modified to include total measurement of all analyte-related peaks.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 80.2 mg/min of coal tar naphtha via a syringe injector to a dry air stream flowing at a rate of 0.0992 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 29.6 mg of coal tar naphtha when a test atmosphere containing 809 mg/cu m of coal tar naphtha in air was sampled at 0.19 liters per minute for 193 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0089 \qquad \overline{CV}_2 = 0.0101 \quad \overline{CV}_T = 0.0513$$

The average recovery of the generated samples over all levels was

$$106 \pm 6.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Naphtha, Coal Tar S86

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.965	1.731	0.881	3.93	3.46	0.880	8.04	6.97	0.867
1.965	1.708	0.869	3.93	3.41	0.868	8.04	6.92	0.861
1.965	1.753	0.892	3.93	3.43	0.873	8.04	6.97	0.867
1.965	1.751	0.891	3.93	3.45	0.878	8.04	7.00	0.871
1.965	1.822	0.927	3.93	3.41	0.868	8.04	7.01	0.872
1.965	1.768	0.900	3.93	3.42	0.870	8.04	6.98	0.868
n =	6			6			6	
mean	0.893			0.873			0.868	
std dev	0.0196			0.00515			0.00388	
CV_1	0.0220			0.00590			0.00448	

$\overline{CV_1}$ 0.0134

$\overline{CV_{A+\overline{DE}}}$ 0.0145

Data Sheet: Naphtha, Coal Tar S86
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.823	2.083	10.09	206.4	192.7	
	1.775	2.029	10.09	201.1	192.7	
	1.845	2.109	10.09	209.0	192.7	
	1.792	2.048	10.09	203.0	192.7	
	1.809	2.067	10.09	204.9	192.7	
	1.834	2.096	10.09	207.7	192.7	
			n = 6			
			mean	205.4		106.6
			std dev	2.96		
			CV_2	0.0144		
1S	3.68	4.21	10.09	417	398	
	3.62	4.14	10.00	414	398	
	3.62	4.14	9.92	417	398	
	3.75	4.29	10.27	418	398	
	3.67	4.19	10.14	413	398	
	3.65	4.17	10.05	415	398	
			n = 6			
			mean	416		104.5
			std dev	1.97		
			CV_2	0.00473		
2S	7.90	9.03	10.41	867	809	
	7.54	8.62	10.14	850	809	
	7.70	8.80	10.14	868	809	
	7.69	8.79	10.09	871	809	
	7.96	9.10	10.50	867	809	
	7.67	8.77	10.14	868	809	
			n = 6			
			mean	865		106.9
			std dev	7.57		
			CV_2	0.00876		
			$\overline{CV_2}$	0.0101		

Backup Data Report

Substance: Propane, No. S87

OSHA Standard: 1800 mg/cu m (1000 ppm)

Chemical used for validation: Propane, Matheson Gas Products

Procedure

An MSA Combustible Gas Indicator, Model 40 was used for the analysis of propane vapor in air. The combustible gas meter was first calibrated by measuring the response (meter reading) of a series of standards containing a known amount of propane. The standards were prepared by dosing a controlled sample chamber (M^3) with known amounts of pure propane. The propane was dispensed from a gas cylinder equipped with a needle valve for controlling flow rate. The flow rate, measured with a soap bubble flowmeter, and the dosing time were used to determine the resultant concentration of propane in the M^3

The M^3 is a rectangular aluminum chamber constructed with dimensions such that its internal volume is 1.00 cu m. The front of the chamber has three 1/4 inch stainless steel fittings and a silicone septum which allows the introduction of gaseous or liquid samples and extraction of air samples for analysis. Shutters are provided at the inlet and exit ends; the inlet is fitted with both a charcoal filter and an absolute particulate filter connected to a blower in series to purify air entering the chamber. A fan blade is mounted inside at the top of the chamber for homogeneous mixing.

The response of a series of ten standard propane concentrations ranging from 200-2000 ppm was measured with the MSA meter using the most sensitive scale, 10% L.E.L. The calibration curve so derived is shown in Figure 1. This calibration curve was used to determine the concentration of propane in the air samples tested. Refer to the Instrument Manual for the details on the proper use of the combustible gas meter.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 208.3 ml/min of propane to a dry air stream flowing at a rate of 0.1033 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 sampling ports at the 3 test levels were analyzed sequentially with the combustible gas meter. Details of the sample generation equipment may be found in the Butyl Acetate S47 Backup Data Report.

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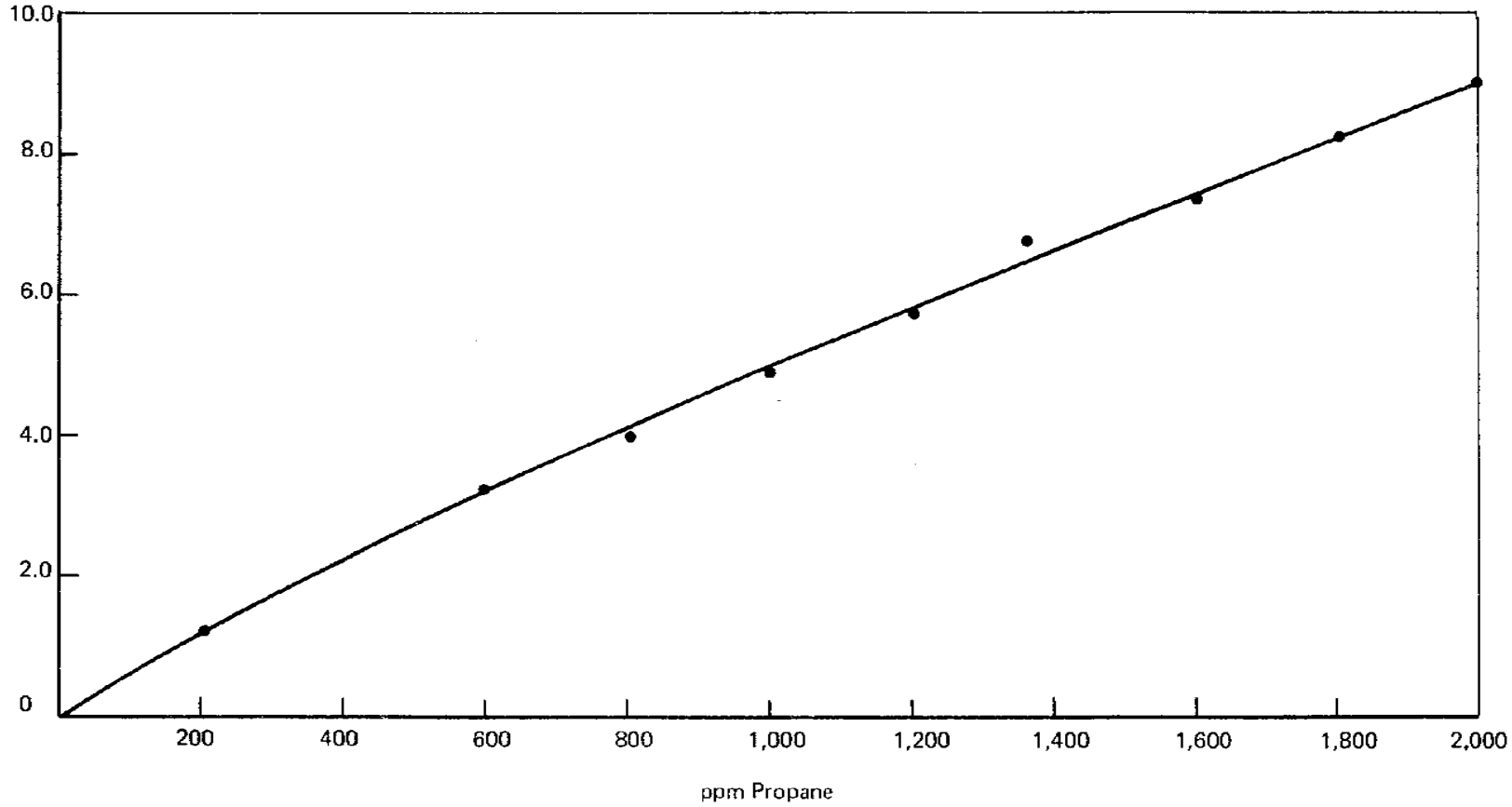


FIGURE 1 CALIBRATION CURVE FOR PROPANE, S87
MSA COMBUSTIBLE GAS INDICATOR, MODEL 40

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_2 = 0.0172 \qquad \overline{\overline{CV}}_T = 0.053$$

The average recovery of the generated samples over all levels was

$$104.9 \pm 6.9\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Instruction Manual, MSA Combustible Gas Indicator, Model 40, Mine Safety Appliance Company, Pittsburgh, Pa.

Data Sheet: Propane, S87

Sampling and Analysis

Test Level	Found		Taken	
	Meter Reading	ppm	ppm	Recovery
0.5S	2.9	535	481	
	2.9	535	481	
	2.9	535	481	
	3.0	555	481	
	2.9	535	481	
	2.8	515	481	
	n = 6			111.2
	mean	535		
	std dev	12.65		
	CV_2	0.0236		
1S	5.0	1010	991	
	5.1	1035	991	
	5.0	1010	991	
	5.0	1010	991	
	5.1	1035	991	
	5.0	1010	991	
	n = 6			102.7
	mean	1018		
	std dev	12.91		
	CV_2	0.0127		
2S	9.4	2100	2016	
	9.2	2050	2016	
	9.2	2050	2016	
	9.3	2070	2016	
	9.1	2020	2016	
	9.2	2050	2016	
	n = 6			100.8
	mean	2057		
	std dev	26.6		
	CV_2	0.0129		
	$\overline{CV}_2$	0.0172		

Backup Data Report

Substance: Turpentine

OSHA Standard: 560 mg/cu m

Chemical used for validation: Turpentine Oil, double rectified, Fisher Scientific Co. (Boiling range: 150-170°C; density: 0.868 g/ml)

Procedure

The general procedure used is described in NIOSH Method No. S88 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of turpentine represented in a 10-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. Turpentine is a mixture of terpenes and all data are based on integrating the total area of relevant peaks. Desorption efficiencies were determined by plotting the DE values obtained for the 0.5X, 1X and 2X the OSHA standard and hand-drawing the best-fit curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 was used but the calibration technique was modified to include total measurement of all analyte-related peaks.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 109 mg/min of turpentine via a syringe injector to a dry air stream flowing at a rate of 0.0985 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 26.5 mg of turpentine when a test atmosphere containing 1107 mg/cu m of turpentine in air was sampled at 0.19 liters per minute for 126 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0132 \qquad \overline{CV}_2 = 0.0220 \quad \overline{CV}_T = 0.0549$$

The average recovery of the generated samples over all levels was

$$99.3 \pm 7.4\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Turpentine S88

Analysis

Level	0.5			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.778	2.997*	1.079*	5.56	5.37	0.966	11.28	10.75	0.953
2.778	2.684	0.966	5.56	5.34	0.960	11.28	10.48	0.929
2.778	2.684	0.966	5.56	5.22	0.939	11.28	10.51	0.932
2.778	2.639	0.950	5.56	5.29	0.951	11.28	10.21	0.905
2.778	2.684	0.966	5.56	5.28	0.950	11.28	10.48	0.929
2.778	2.729	0.982	5.56	5.25	0.944	11.28	10.51	0.932

n =	5	6	6
mean	0.966	0.952	0.930
std dev	0.0114	0.00997	0.0153
CV_1	0.0118	0.0105	0.0164

$\overline{CV_1}$ 0.0132

$\overline{CV_{A+\overline{DE}}}$ 0.0143

* These values excluded from statistical analysis

Data Sheet: Turpentine S88
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.411	2.541	10.04	253.1	263.8	
	2.427	2.557	10.04	254.7	263.8	
	2.465	2.597	10.04	258.7	263.8	
	2.480	2.613	10.04	260.3	263.8	
	2.442	2.573	10.04	256.3	263.8	
	2.496	2.630	10.04	262.0	263.8	
			n = 6			
			mean	257.5		97.6
			std dev	3.41		
			CV_2	0.0132		
1S	5.11	5.38	10.04	536	544	
	5.07	5.34	9.95	537	544	
	5.07	5.34	9.86	542	544	
	5.42	5.71	10.21	559	544	
	5.21	5.49	10.08	545	544	
	5.25	5.53	9.99	554	544	
			n = 6			
			mean	546		100.4
			std dev	9.27		
			CV_2	0.0170		
2S	11.08	11.68	10.35	1129	1107	
	10.42	10.98	10.08	1089	1107	
	10.79	11.37	10.08	1128	1107	
	10.67	11.24	10.04	1120	1107	
	11.13	11.73	10.44	1123	1107	
	9.96	10.50	10.08	1041	1107	
			n = 6			
			mean	1105		99.8
			std dev	34.7		
			CV_2	0.0314		
			$\overline{CV}_2$	0.0220		

Backup Data Report

Substance: Heptane

OSHA Standard: 2000 mg/cu m

Chemical used for validation: Heptane, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S89 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of heptane represented in a 4 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 408 mg/min of heptane via a syringe injector to a dry air stream flowing at a rate of 0.1005 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 24.7 mg of heptane when a test atmosphere containing 4060 mg/cu m of heptane in air was sampled at 0.19 liters per minute for 32 minutes; breakthrough was observed at this time, i.e., concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for heptane as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 9.92 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for heptane show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0161 \qquad \overline{CV}_2 = 0.0233 \quad \overline{CV}_T = 0.0556$$

The average recovery of the generated samples over all levels was

$$93.5 \pm 7.9\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Heptane S89

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.08	4.03	0.988	8.15	8.12	0.996	16.31	15.66	0.960
4.08	3.93	0.963	8.15	7.86	0.964	16.31	15.60	0.956
4.08	3.90	0.956	8.15	7.76	0.952	16.31	15.47	0.948
4.08	3.83	0.939	8.15	7.76	0.952	16.31	15.54	0.953
4.08	*	*	8.15	7.65	0.939	16.31	15.55	0.953
4.08	3.87	0.949	8.15	7.80	0.957	16.31	15.51	0.951

n =	5	6	6
mean	0.959	0.960	0.954
std dev	0.0185	0.0194	0.00414
CV_1	0.0193	0.0203	0.00433

$\overline{CV}_1$ 0.0161

$\overline{CV}_{A+\overline{DE}}$ 0.0174

*Lost Sample

Data Sheet: Heptane S89
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.53	3.68	4.09	900	968	
	3.36	3.51	4.09	858	968	
	3.53	3.68	4.09	900	968	
	3.54	3.70	4.09	905	968	
	3.26	3.40	4.09	831	968	
	3.56	3.72	4.09	910	968	
			n = 6			
			mean	884		91.3
			std dev	32.0		
			CV_2	0.0362		
1S	7.40	7.72	4.09	1888	1996	
	7.20	7.52	4.05	1857	1996	
	7.21	7.53	4.02	1873	1996	
	7.45	7.78	4.16	1870	1996	
	7.32	7.64	4.11	1859	1996	
	7.21	7.53	4.07	1850	1996	
			n = 6			
			mean	1866		93.5
			std dev	13.67		
			CV_2	0.00733		
2S	15.53	16.21	4.22	3840	4060	
	15.63	16.32	4.11	3970	4060	
	15.38	16.05	4.11	3905	4060	
	15.29	15.96	4.09	3902	4060	
	15.41	16.09	4.25	3786	4060	
	15.32	15.99	4.11	3891	4060	
			n = 6			
			mean	3882		95.6
			std dev	62.8		
			CV_2	0.0162		
			$\overline{CV}_2$	0.0233		

Backup Data Report

Substance: Hexane

OSHA Standard: 1800 mg/cu m

Chemical used for
validation: n-Hexane, Fisher 99 Mol % Pure

Procedure

The general procedure used is described in NIOSH Method No. S90 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of hexane represented in a 4-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 376 mg/min of hexane via a syringe injector to a dry air stream flowing at a rate of 0.1022 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 21.7 mg of hexane when a test atmosphere containing 3679 mg/cu m of hexane in air was sampled at 0.19 liters per minute for 31 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0139 \qquad \overline{CV}_2 = 0.0368 \qquad \overline{CV}_T = 0.0623$$

The average recovery of the generated samples over all levels was

$$97.9 \pm 8.1\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Date Sheet: Hexane S90

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.56	3.48	0.978	7.25	6.88	0.949	14.50	13.86	0.956
3.56	3.33	0.935	7.25	6.84	0.943	14.50	13.81	0.952
3.56	3.35	0.941	7.25	6.85	0.945	14.50	13.65	0.941
3.56	3.36	0.944	7.25	6.98	0.963	14.50	13.98	0.964
3.56	3.32	0.933	7.25	6.75	0.931	14.50	13.68	0.943
3.56	3.34	0.938	7.25	6.73	0.928	14.50	13.75	0.948
n =		6			6			6
mean		0.945			0.943			0.951
std dev		0.0167			0.0127			0.0086
CV_1		0.0177			0.0135			0.0090

$\overline{CV}_1$ 0.0139

$\overline{CV}_{A+\overline{DE}}$ 0.0150

Data Sheet: Hexane S90
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.29	3.48	3.97	877	877	
	3.25	3.44	3.97	867	877	
	1.53*	1.62*	3.97	409*	877	
	3.10	3.28	3.97	826	877	
	2.93	3.10	3.97	780	877	
	3.25	3.44	3.97	867	877	
			n = 5			
			mean	843		96.1
			std dev	40.5		
			CV_2	0.0481		
1S	6.37	6.73	3.97	1695	1808	
	6.42	6.79	3.94	1723	1808	
	6.56	6.93	3.90	1777	1808	
	6.89	7.28	4.01	1815	1808	
	6.09	6.44	3.96	1626	1808	
	6.64	7.02	3.89	1805	1808	
			n = 6			
			mean	1740		96.2
			std dev	72.8		
			CV_2	0.0418		
2S	13.97	14.77	4.06	3640	3680	
	14.14	14.95	3.96	3780	3680	
	14.14	14.95	3.96	3780	3680	
	13.98	14.78	3.94	3750	3680	
	14.61	15.44	4.10	3770	3680	
	14.05	14.85	3.96	3750	3680	
			n = 6			
			mean	3745		101.6
			std dev	53.2		
			CV_2	0.0142		
			$\overline{CV}_2$	0.0368		

Backup Data Report

Substance: Butadiene

OSHA Standard: 2200 mg/cu m

Chemical used for validation: 1,3-Butadiene, Matheson C.P.

Procedure

The general procedure used is described in NIOSH Method No. S91 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of a solution of butadiene in carbon disulfide so as to represent an amount equivalent to a 1-liter air sample. The spiking solution was prepared by bubbling butadiene into carbon disulfide and determining the butadiene concentration by gas chromatographic analysis on a 6-ft x 1/8-in stainless steel column using butadiene gas calibration standards. The solution containing 68.38 mg/ml was found to be stable over the three day period it was used. Appropriate calibration standards for GC analysis were prepared using this butadiene solution as well as pentane calibration standards. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 199.5 ml/min (450.2 mg/min) of butadiene via a syringe injector to a dry air stream flowing at a rate of 0.0980 cu m/min. The three sample lines were then maintained at dilution ratios of 0.232, 0.495 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the three test levels were collected simultaneously at 0.067 liters per minute for 20 minutes(1 liter). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 7.9 mg of butadiene when a test atmosphere containing 4370 mg/cu m of butadiene in air was sampled at 0.19 liters per minute for 9.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data were obtained under different operating conditions.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0252 \qquad \overline{CV}_2 = 0.0268 \quad \overline{CV}_T = 0.0577$$

The average recovery of the generated samples over all levels was

$$100.1 \pm 7.4\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Butadiene S91

Analysis

Level	0.5S			1S			2S		
	mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
	0.889	0.790	0.889	1.778	1.602	0.901	3.420	2.902	0.849
	0.889	0.794	0.893	1.778	1.577	0.887	3.420	3.024	0.884
	0.889	0.782	0.880	1.778	1.608	0.904	3.420	2.873	0.840
	0.889	0.790	0.889	1.778	1.603	0.902	3.420	2.686	0.785
	0.889	0.809	0.910	1.778	1.577	0.887	3.420	2.950	0.863
	0.889	0.812	0.913	1.778	1.594	0.897	3.420	2.829	0.827
n		6			6			6	
mean		0.896			0.896			0.841	
std dev		0.0130			0.00758			0.0339	
CV_1		0.0145			0.00846			0.0403	

$\overline{CV_1}$ 0.0252

$\overline{CV_{A+\overline{DE}}}$ 0.0272

Data Sheet: Butadiene S91
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.256	1.431	1.33	1076	1065	
	1.276	1.453	1.31	1109	1065	
	1.343	1.530	1.39	1101	1065	
	1.382	1.574	1.43	1101	1065	
	1.360	1.549	1.44	1076	1065	
	1.241	1.413	1.41	1002	1065	
			n = 6			
			mean	1078		101.2
			std dev	39.5		
			CV_2	0.0366		
1S	2.696	3.071	1.35	2275	2274	
	2.625	2.990	1.33	2248	2274	
	2.624	2.989	1.33	2247	2274	
	2.608	2.970	1.30	2285	2274	
	2.441	2.780	1.31	2122	2274	
	2.546	2.900	1.31	2214	2274	
			n = 6			
			mean	2232		98.2
			std dev	59.3		
			CV_2	0.0266		
2S	5.33	6.07	1.30	4669	4590	
	5.40	6.15	1.31	4695	4590	
	5.45	6.21	1.33	4669	4590	
	5.72	6.51	1.41	4617	4590	
	5.23	5.96	1.30	4585	4590	
	5.27	6.00	1.31	4580	4590	
			n = 6			
			mean	4636		101.0
			std dev	48.5		
			CV_2	0.0105		
			$\overline{CV}_2$	0.0268		

Backup Data Report

Substance:	Ketene, S92
OSHA Standard:	0.9 mg/cu m
Chemical used for validation:	Diketene, Technical Grade, Aldrich Chemical Company, Inc.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of ketene in air is described in NIOSH Method S92, which has been adapted from References 1 and 2. Collection efficiency tests were done at 2 times the OSHA standard. Samples of ketene in dry air were generated by the procedure described below, and bubbler samples were collected in 10 ml of the alkaline hydroxylammonium chloride absorbing solution. The details of the analytical method are described in NIOSH Method S92.

The concentration of ketene in the air sampled was determined by dividing the amount found by the collection efficiency and the volume of air collected.

Modification of Reference 1

The concentrations of the sodium hydroxide, hydroxylammonium chloride, and the ferric chloride solutions used for these studies have been decreased to half of the original level recommended in Reference 1. Initial studies showed high reagent blank levels when the original reagent concentrations recommended in Reference 1 were used. The total volume of reagents used was also decreased for increased sensitivity.

Analysis

Ketene is unstable and difficult to handle except under unusual conditions. Further,it is difficult to obtain ketene of known purity (Reference 4). For these reasons the validation of the analytical method was done using ethyl acetate for spiking and for the preparation of the calibration curve. The chemistry of color formation is reported to be the same for esters and ketene (Reference 1).

Generation

The basic procedure used to generate ketene vapor was to thermally decompose diketene in a tube furnace. The vapor generation/dilution system described in the S47 Butyl Acetate Backup Data Report was modified as shown schematically in Figure 1.

Diketene was purified using the distillation procedure given in Reference 4. Initial generation experiments were conducted using pure diketene. However, because the delivery rate was so low, about

0.0002 ml/min, we were unable to arrive at a measured concentration level within 25% of the target level. Therefore the final experiments were conducted using a 1.65% (w/w) solution of diketene in hexane. The tube furnace was operated at 600± 50°C. The diketene/hexane solution was added at the entrance to the tube furnace to a quartz tube which had been packed with broken Pyrex tubing. By pumping a portion of the Main Line air through the tube furnace, the reaction products were swept into the dilution line. No net change in the calibration air flow occurred because the same amount of air was removed and returned. The heated section of the quartz tube was approximately 30 cm long and it had an ID of 2 cm. Experiments were done using hexane only to be sure that use of this solvent did not lead to some background interference. No color formation was observed in the reaction solutions for these studies.

The concentration of ketene generated was determined by collecting the vapor in the hydroxylammonium chloride solution using the midget fritted glass bubblers and measuring the concentration against the calibration curve. By running collection efficiency tests using a set of two bubblers in series, we determined that the bubblers were 94.4% efficient. This factor was used to correct the observed concentration.

The 1.65% diketene solution was delivered at a rate of 12.3 mg/min (0.203 mg diketene/min) to the dry air stream flowing at a rate of 0.0989 cu m/min at 23°C and 757 mm of Hg. The 2S level collection experiments found an efficiency corrected concentration of 1.74 mg/cu m of ketene. This calculates to an 85% yield of ketene from diketene in the tube furnace. Yields reported in Reference 4 using high concentrations of diketene at 550°C vary from 46-55%.

The dilution ratios of the three sample lines were maintained at 0.232, 0.495, and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 45 minutes (50 liters).

Collection Efficiency

The collection efficiency was determined by sampling the six lines at the 2S concentration level. A pair of bubblers connected in series was used at each sampling line. Tests were done for air sample concentrations of 1.64 mg/cu m and 1.74 mg/cu m at a sampling rate of 1.1 liters per minute for 45 minutes. Each bubbler was analyzed separately and the relative amount of ketene collected in the primary and backup bubblers was determined, based on the total mg found in both bubblers. From the two sets of such experiments conducted (12 samples), the average collection efficiency in the first bubbler is 94.4 ±4.1%. (See Table 1)

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.0523 \qquad \overline{CV}_2 = 0.0451 \qquad \overline{CV}_T = 0.0639$$

The average recovery of the generated samples over all levels was

$$97.2 \pm 8.6\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

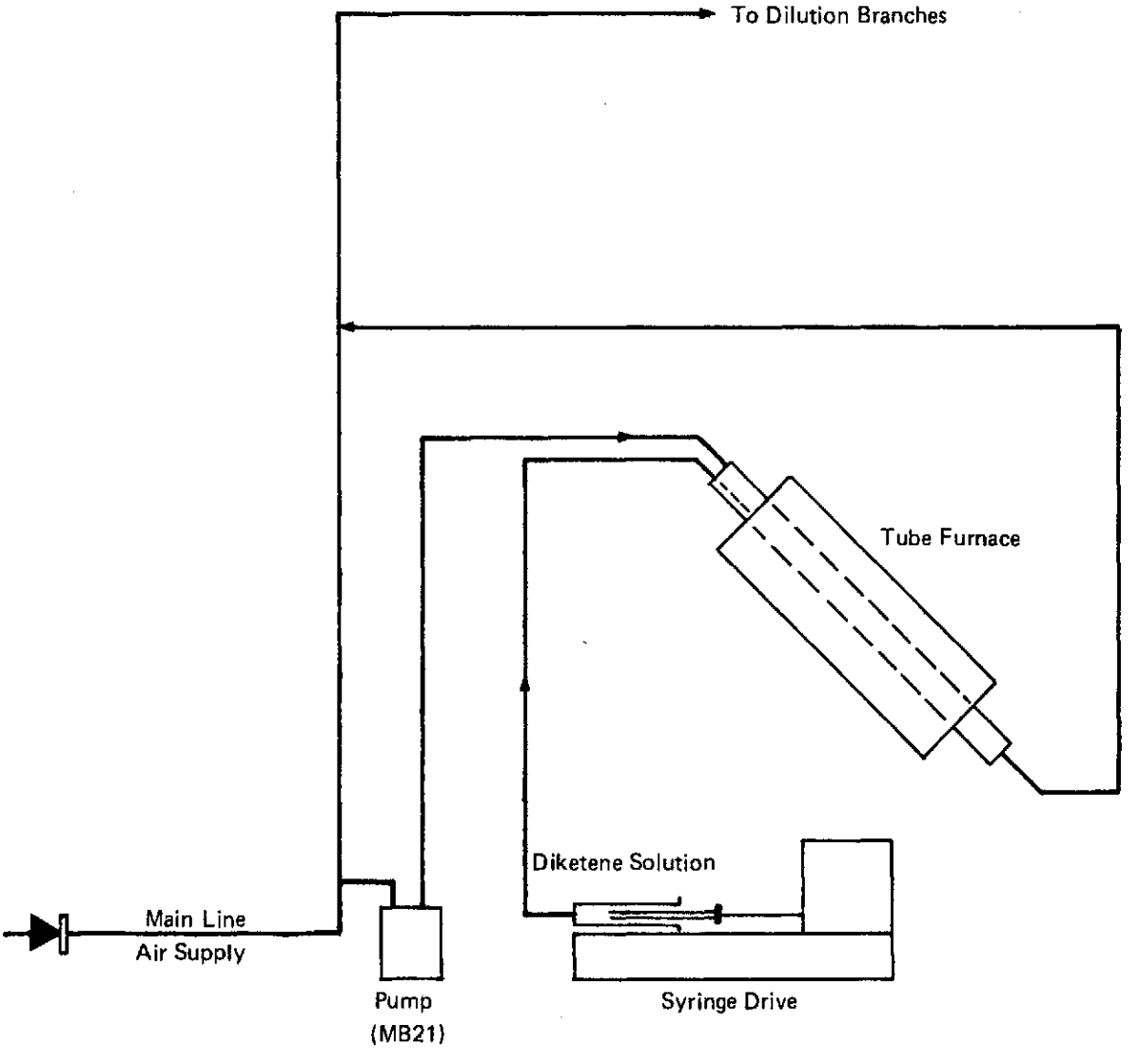
References

1. Hanson, N.W., D.A. Reilly, H.E. Stagg, eds., The Determination of Toxic Substances in Air, W. Heffer & Sons Ltd., Cambridge, England, pp. 152-156, 1965.

2. Diggle, W.M. and J.C. Gage, Analyst 78, 473, (1953).

3. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

4. Dauben, W.G., Editor-in-Chief, Organic Syntheses, Vol. 45, John Wiley & Sons, New York, p. 50, 1965.



KETENE GENERATOR

TABLE I

Collection Efficiency Data

2S Concentration Level (mg/cu m)	µg Collected in Bubbler First	Second	Total	% in First	
1.64	75	3	78	96.2	
	65	9	74	87.8	
	65	9	74	87.8	
	72	10	82	87.8	
	74	5	79	93.7	
	76	2	78	97.4	
				91.8	± 4.52
1.74	76	3.5	79.5	95.6	
	82	2.6	84.6	96.9	
	80	2.6	82.6	96.9	
	83	2.6	85.6	97.0	
	79	2.0	81.0	97.5	
	85	2.0	87.0	97.7	
				96.9	±0.73

Overall Average Collection Efficiency 94.4 ± 3.6%

Data Sheet: Ketene[1] S92

Analysis

Level	0.5S			1S			2S	
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
0.021	0.019	90.5	0.043	0.045	104.7	0.086	0.089	103.5
0.021	0.021	100.0	0.043	0.043	100.0	0.086	0.083	96.5
0.021	0.020	95.2	0.043	0.043	100.0	0.086	0.088	102.3
0.021	0.023	109.5	0.043	0.042	97.7	0.086	0.078	90.7
0.021	0.022	104.8	0.043	0.044	102.3	0.086	0.083	96.5
0.021	0.022	104.8	0.043	0.046	107.0	0.086	0.084	97.7
n =		6			6			6
mean		100.8			101.9			97.9
std dev		7.01			3.43			4.62
CV_1		0.0696			0.0337			0.0471

$\overline{CV}_1$ 0.0523

$\overline{CV}_{A+\overline{DE}}$ 0.0565

[1] Ethyl acetate was used for spiking in amounts equivalent to the values reported as mg of ketene (1 mole ethyl acetate = 1 mole ketene).

Data Sheet: Ketene, S92
Sampling and Analysis

Test Level	Found				Taken[Δ]	Recovery*,[Δ]
	mg	Corr mg*	Liters	mg/cu m	mg/cu m	
0.5S	0.018	0.019	49.6	0.38	0.40	
	0.018	0.019	49.0	0.39	0.40	
	0.017	0.018	49.8	0.36	0.40	
	0.019	0.020	50.9	0.39	0.40	
	0.018	0.019	50.0	0.38	0.40	
	0.018	0.019	49.0	0.39	0.40	
			n = 6			
			mean	0.38		95.0
			std dev	0.0117		
			CV_2	0.0308		
1S	0.035	0.037	49.0	0.76	0.86	
	0.039	0.041	49.4	0.83	0.86	
	0.039	0.041	49.4	0.83	0.86	
	0.040	0.043	49.8	0.86	0.86	
	0.042	0.045	49.8	0.90	0.86	
	0.037	0.039	49.6	0.79	0.86	
			n = 6			
			mean	0.83		96.5
			std dev	0.0496		
			CV_2	0.0597		
2S	0.076	0.081	49.6	1.63	1.74	
	0.082	0.087	49.4	1.76	1.74	
	0.080	0.085	49.0	1.73	1.74	
	0.083	0.088	49.4	1.78	1.74	
	0.079	0.084	49.4	1.70	1.74	
	0.085	0.090	49.2	1.83	1.74	
			n = 6			
			mean	1.74		100
			std dev	0.0691		
			CV_2	0.0397		
			$\overline{CV_2}$	0.0451		

* Corrected for collection efficiency found at 2S level.

Δ Based on 100% Recovery at 2S level and appropriate dilution ratio at 0.5S and 1S levels

Backup Data Report

Substance: LPG (Liquified Petroleum Gas), No. S93

OSHA Standard: 1000 ppm

Chemical used for validation: LPG, Pyrofax Corporation

Procedure

A Davis Vapotester Model M-6 or an equivalent dual range explosive gas meter is recommended for the analysis of LPG. The accuracy of the MSA combustible Gas Indicator Model 40 was inadequate for LPG analysis.

The MSA Combustible Gas Indicator was initially used for the analysis of LPG vapor in air. The MSA meter was calibrated with a series of ten LPG standards in duplicate at concentrations ranging from 200-2000 ppm. The M^3 was used for the calibration in the same manner described in detail in the Propane S87 Backup Data Report. The calibration curve so derived is shown in Figure 1. The data obtained, when the calibrated MSA meter was used to analyze two sets of 18 generated samples, were not satisfactory because the data were precise but inaccurate. The recovery values obtained were unusually high, averaging 122 ± 15% as shown in Table 1. This observation could be due to difficulties in taking readings at the low end of the MSA - 10% L.E.L. scale; note the relative spread of data points in the calibration curve, Figure 1.

A Davis Vapotester Model M-6 was subsequently tested for suitability for LPG analysis. The Davis meter was calibrated in the same manner described previously and the calibration curve is shown in Figures 2 and 3 for the 10:1 and 1:1 scales respectively. These calibration curves were used to determine the concentration of LPG in the air samples tested. The details on the proper use of the Davis Vapotester may be found in the instrument instruction manual.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 201.6 ml/min of LPG to a dry air stream flowing at a rate of 0.1005 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 sampling ports at the 3 test levels were analyzed sequentially with the combustible gas meter. Details of the sample generation equipment may be found in the Butyl Acetate S47 Backup Data Report.

Table 1

LPG Analysis Data with MSA Model 40

	----------ppm Found----------		
Test Level	0.5S	1S	2S
Trial 1	640	1060	2060
	640	1060	2060
	620	1060	2080
	590	1060	2080
	590	1060	2080
	620	1060	2080
Average	620 ± 23	1060 ± 0	2070 ± 10
ppm Taken	463	955	1942
% Recovery	134	111	107
Trial 2	650	1080	2000
	620	1080	2000
	620	1080	2020
	620	1080	2050
	600	1080	2020
	600	1080	2050
Average	620 ± 16	1080 ± 0	2020 ± 23
ppm Taken	431	887	1806
% Recovery	144	122	112

Overall Average Recovery = 122 ± 15%

383<

3841

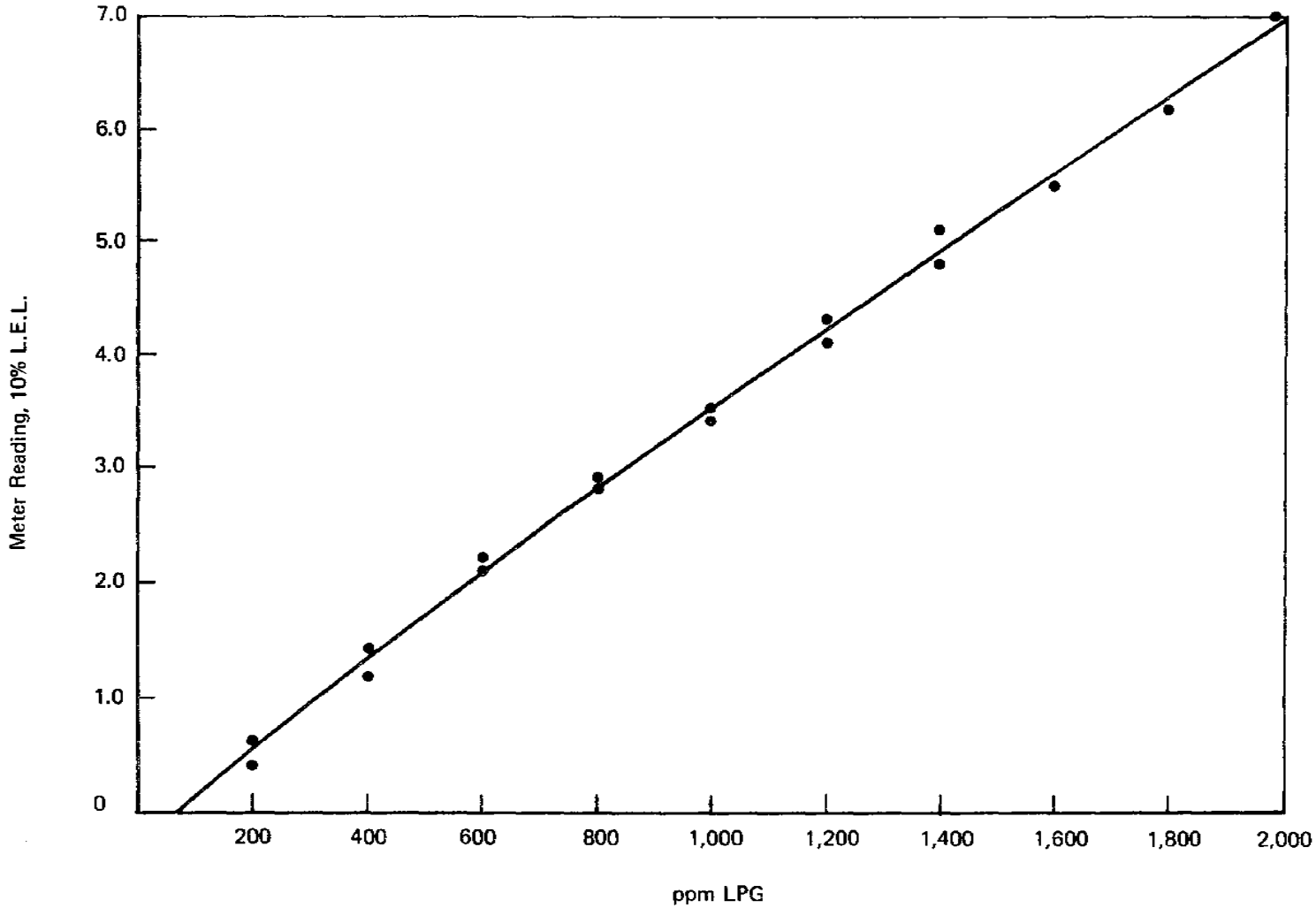


FIGURE 1 CALIBRATION CURVE FOR LPG, S93
MSA COMBUSTIBLE GAS INDICATOR, MODEL 40

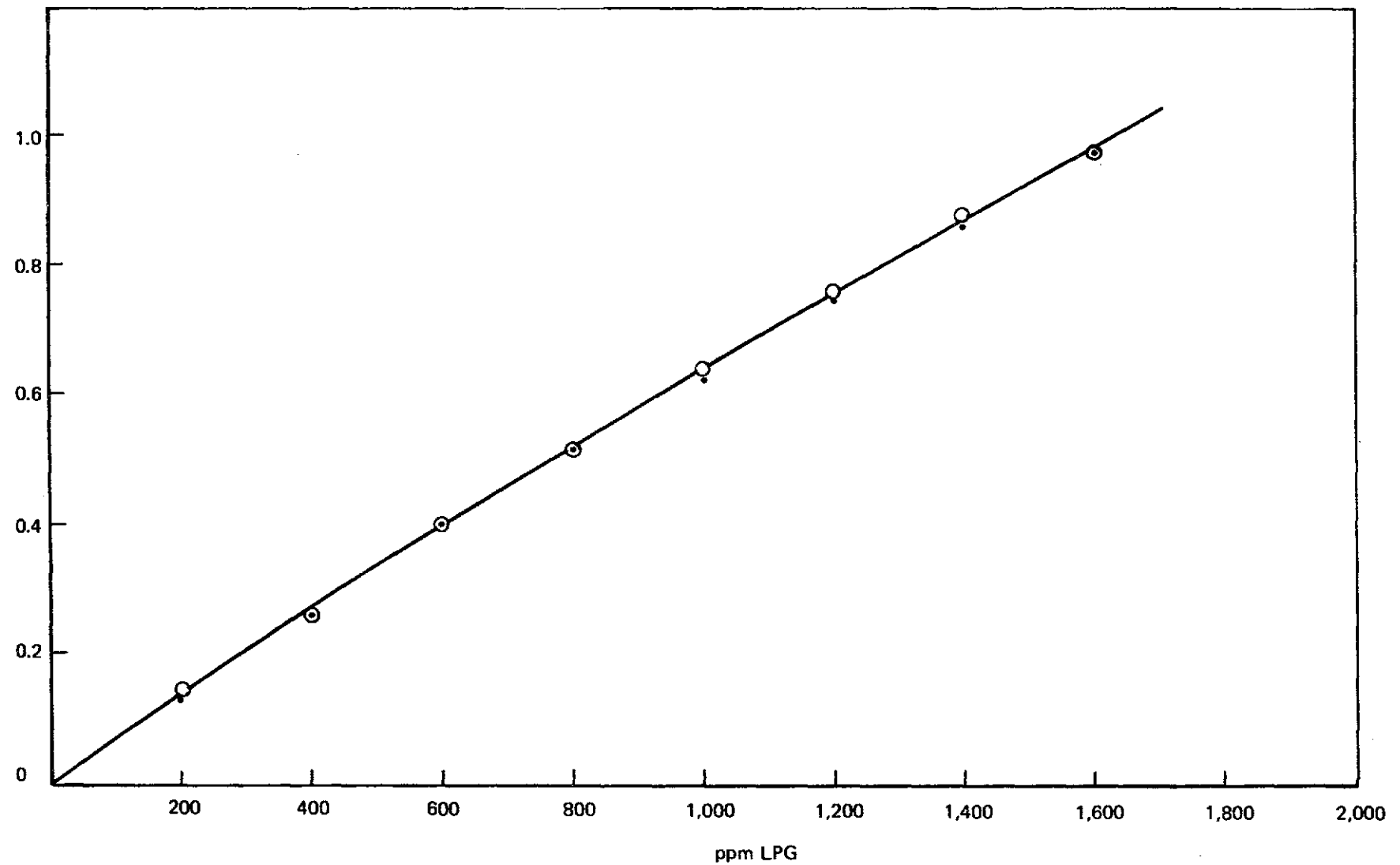
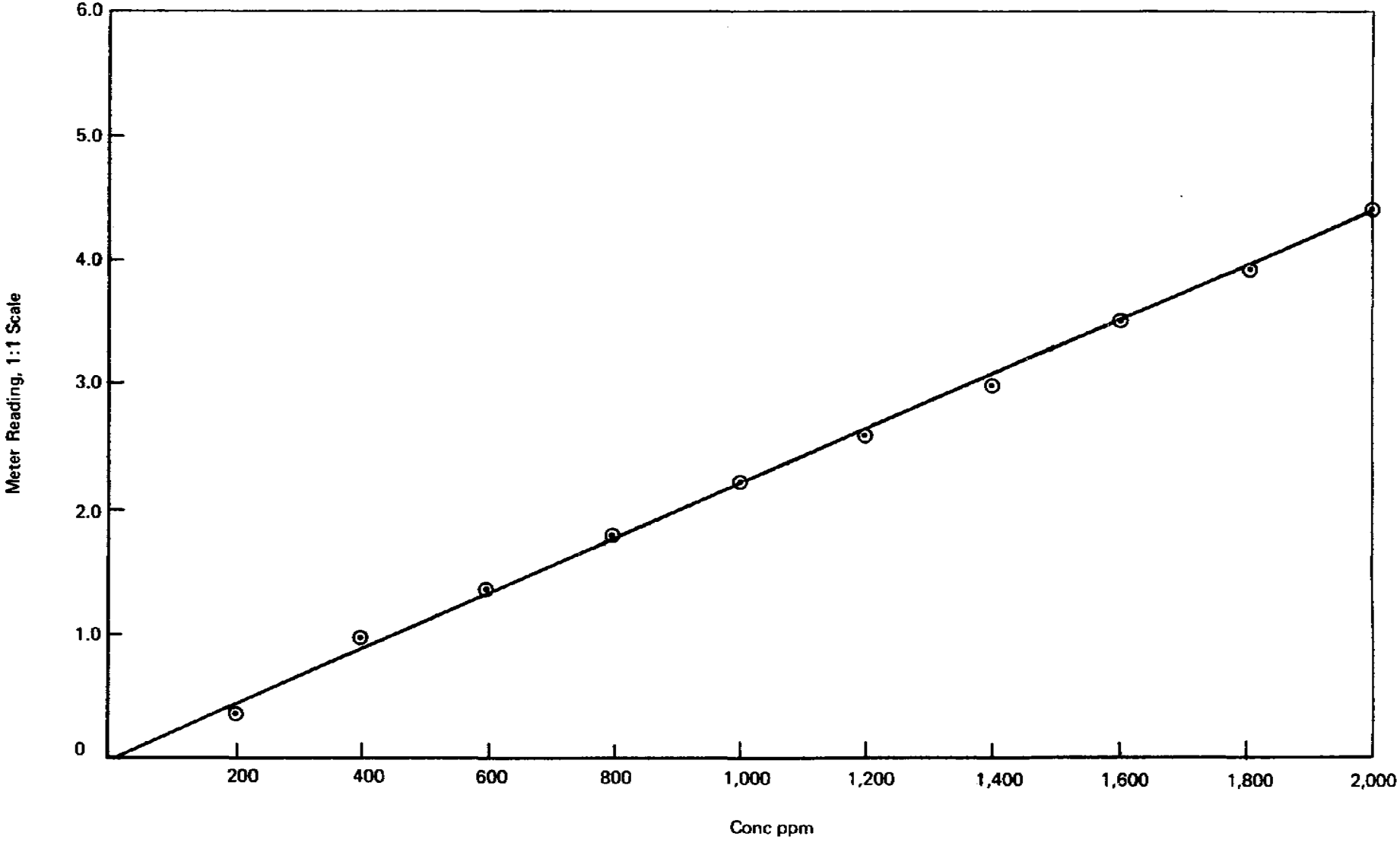


FIGURE 2 CALIBRATION CURVE FOR LPG, S93
DAVIS VAPOTESTER MODEL M6

S93-4



S93-5

FIGURE 3 CALIBRATION CURVE FOR LPG, S93
DAVIS VAPOTESTER MODEL M6

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_2 = 0.0084 \qquad \overline{CV}_T = 0.051$$

The average recovery of the generated samples over all levels was

$$91.3 \pm 0.5\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Instruction Manual, Davis Vapotester Model M-6, Davis Instruments, 45 Halleck Street, Newark, N.J.

Data Sheet: LPG, S93
Sampling and Analysis
(Davis Vapotester, Model M-6)

Test Level	Found		Taken	
	Meter Reading	ppm	ppm	Recovery
0.5S (10:1 Scale)	0.27	410	478	
	0.28	425	478	
	0.28	425	478	
	0.28	425	478	
	0.28	425	478	
	0.28	425	478	
		n = 6		88.5
		mean 423		
		std dev 6.12		
		CV_2 0.0145		
1S (1:1 Scale)	2.0	920	986	
	2.0	920	986	
	2.0	920	986	
	2.0	920	986	
	2.0	920	986	
	2.0	920	986	
		n = 6		93.3
		mean 920		
		std dev 0.0		
		CV_2 0.0		
2S (1:1 Scale)	4.1	1850	2006	
	4.1	1850	2006	
	4.1	1850	2006	
	4.1	1850	2006	
	4.1	1850	2006	
	4.1	1850	2006	
		n = 6		92.2
		mean 1850		
		std dev 0.0		
		CV_2 0.0		
		$\overline{CV}_2$ 0.0084		

Backup Data Report

Substance: Methylcyclohexane

OSHA Standard: 2000 mg/cu m

Chemical used for validation: Methylcyclohexane, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S94 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methylcyclohexane represented in a 4-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 402 mg/min of methylcyclohexane via a syringe injector to a dry air stream flowing at a rate of 0.1020 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 24 mg of methylcyclohexane when a test atmosphere containing 3941 mg/cu m of methylcyclohexane in air was sampled at 0.19 liters per minute for 32 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0116 \qquad \overline{CV}_2 = 0.0143 \qquad \overline{CV}_T = 0.0522$$

The average recovery of the generated samples over all levels was

$$106.1 \pm 6.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methylcyclohexane S94

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.98	3.83	0.962	7.65	7.09	0.927	16.07	15.46	0.962
3.98	4.54*	1.141*	7.65	7.17	0.937	16.07	15.62	0.972
3.98	3.82	0.960	7.65	7.27	0.950	16.07	15.28	0.951
3.98	3.72	0.935	7.65	7.27	0.950	16.07	15.69	0.976
3.98	3.85	0.967	7.65	7.24	0.946	16.07	15.38	0.957
3.98	3.85	0.967	7.65	7.27	0.950	16.07	13.86*	0.862*
n =		5			6			5
mean		0.958			0.943			0.964
std dev		0.0133			0.0095			0.0104
CV_1		0.0139			0.0100			0.0108

$\overline{CV_1}$ 0.0116

$\overline{CV_{A+\overline{DE}}}$ 0.0125

* These values excluded from statistical analysis

Data Sheet: Methylcyclohexane S94
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.77	3.99	3.97	1005	940	
	3.72	3.94	3.97	992	940	
	3.73	3.95	3.97	995	940	
	3.77	3.99	3.97	1005	940	
	3.79	4.01	3.97	1010	940	
	3.82	4.05	3.97	1020	940	
			n = 6			
			mean	1005		106.9
			std dev	10.17		
			CV_2	0.0101		
1S	7.69	8.09	3.97	2038	1937	
	7.69	8.09	3.93	2059	1937	
	7.66	8.06	3.90	2067	1937	
	7.93	8.35	4.04	2067	1937	
	7.84	8.25	3.99	2068	1937	
	7.35	7.74	3.95	1959	1937	
			n = 6			
			mean	2043		105.5
			std dev	42.7		
			CV_2	0.0209		
2S	16.41	17.00	4.09	4160	3940	
	16.30	16.89	3.99	4230	3940	
	15.99	16.60	3.99	4160	3940	
	15.94	16.55	3.97	4170	3940	
	16.79	17.40	4.13	4210	3940	
	15.86	16.47	3.99	4130	3940	
			n = 6			
			mean	4180		106.1
			std dev	36.7		
			CV_2	0.00878		
			$\overline{CV}_2$	0.0143		

BACKUP DATA REPORT

Substance:	Propylene Dichloride S95
OSHA Standard:	75 ppm (350 mg/cu m)
Chemical used for validation:	Propylene Dichloride, Technical Grade Carbide and Carbon Chemicals Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with an 875 mg/ml solution of propylene dichloride in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10-liter air sample at the respective level. The eluting solvent was carbon disulfide. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-undecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels were not in the proper order and differed by less than one standard deviation, therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with one modification. An internal standard was added for improved accuracy.

Generation

The test atmosphere was generated by a syringe injection technique. The three concentrations were obtained by sampling only at the first stage and repeating the generation at a different rate of propylene dichloride injection. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate was 24.2 liters per minute, and the rate of propylene dichloride injection was 0.9356, 0.4375, and 0.1898 g/hr respectively for 2, 1, and 0.5 times the OSHA standard levels. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

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Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 586 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simulaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred after 1 hour, 30 minutes. Thus the capacity of this lot of charcoal is 10.5 mg of propylene dichloride and at the recommended sampling rate, the breakthrough volume is 18 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV_1} = 0.0173 \qquad \overline{CV_2} = 0.0248 \qquad \overline{CV_T} = 0.0559$$

The average recovery of the generated samples over all levels was:

99.6%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Propylene Dichloride S95

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.750	1.673	0.956	3.500	3.375	0.964	7.000	6.665	0.952
1.750	1.668	0.953	3.500	3.305	0.944	7.000	6.723	0.960
1.750	1.668	0.953	3.500	3.412	0.975	7.000	6.804	0.972
1.750	1.738	0.993	3.500	3.462	0.989	7.000	6.822	0.975
1.750	1.712	0.978	3.500	3.511	1.003	7.000	6.862	0.980
1.750	1.722	0.984	3.500	3.397	0.971	7.000	6.839	0.977
n =		6			6			6
mean		0.970			0.974			0.969
std dev		0.0179			0.0203			0.0108
CV_1		0.0184			0.0208			0.0112

CV_1 0.0173

$\overline{CV}_{A+\overline{DE}}$ 0.0187

Data Sheet: Propylene Dichloride S95

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.286	1.324	9.600	137.9	133	103.7
	1.317	1.356	9.600	141.3	133	106.2
	1.240	1.278	9.250	138.1	133	103.8
	1.354	1.395	9.600	145.3	133	109.3
	1.214	1.250	8.900	140.5	133	105.6
	1.292	1.331	9.400	141.6	133	106.5
			n = 6			
			mean	140.8		105.9
			std dev	2.7		
			CV_2	0.0193		
1S	2.821	2.906	9.150	317.6	308	103.1
	2.979	3.068	10.250	299.4	308	97.2
	3.058	3.149	10.050	313.4	308	101.7
	2.630	2.709	9.100	297.6	308	96.6
	2.900	2.987	9.550	312.7	308	101.5
	2.716	2.797	9.100	307.4	308	99.8
			n = 6			
			mean	308.0		100.0
			std dev	8.1		
			CV_2	0.0262		
2S	6.201	6.387	10.850	588.7	667	88.3
	5.902	6.079	9.700	626.7	667	94.0
	5.717	5.889	9.400	626.4	667	93.9
	5.746	5.919	9.300	636.4	667	95.4
	6.212	6.398	10.150	630.3	667	94.5
	5.854	6.030	9.850	612.1	667	91.8
			n = 6			
			mean	620.1		93.0
			std dev	17.3		
			CV_2	0.0280	$\overline{CV}_2$	0.0248

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Backup Data Report

Substance:	Pentachloronaphthalene, No. S96
OSHA Standard:	0.5 mg/cu m - skin
Chemical Used for Validation:	Pentachloronaphthalene Koppers

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S96. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 270-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (6, 12, and 24 microliters) of a 112.05 mg/10 ml solution of pentachloronaphthalene in benzene were spiked onto 37-mm glass fiber filters. The analyte was extracted from the filters with 15 ml of iso-octane and analyzed by gas chromatography with an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S96.

Test atmospheres of pentachloronaphthalene at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type A glass fiber filters connected in series with a midget bubbler containing 15 ml of iso-octane.

Generation

Samples of pentachloronaphthalene were generated by the procedure described in Reference No. 1. A solution of pentachloronaphthalene in toluene (5 g/liter) was used in the aspiration system. A pressure drop of 8 psi across the aspirator tip was used in the generation. It is estimated that the particles had a median diameter of 1.0 micron.

The output of the aspirator was diluted with an appropriate amount of air to obtain the 2X concentration. This level was further diluted to the 1X and 0.5X levels, and samples were collected simultaneously at all three levels. The dilution system is described in Reference No. 2. Samples were collected for 201 minutes at a flow rate of approximately 1.3 liter/minute.

It was not possible to get a direct measure of the "taken" concentration of pentachloronaphthalene. Thus the mean of the "found" concentration was used as a measure of the concentration in the sampling system. The means for the three sampling chambers were found to be 1.541, 0.650, and 0.293 mg/cu m. The dilution ratios were expected to be 1/0.5/0.25, the lower ratios (1/0.42/0.19) were likely the result of losses in the system rather than due to bias in the method.

Collection Efficiency

Collection efficiency was determined at a concentration of 1.541 mg/cu m by connecting a filter and two midget bubblers (each containing 15 ml of iso-octane) in series. This experiment was performed on each of the 6 samples taken for validation at the 2X level. Samples were collected for 201 minutes at a flow rate of 1.3 liters per minute. The collection efficiency of the single filter and bubbler was determined to be 1.00 since no pentachloronaphthalene was detected in any of the second bubblers at a detection limit of 0.015 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below.

Total Concentration found in the filter and first bubbler	Concentration found in second bubbler	Collection Efficiency
1.388 mg/cu m	N.D.*	1.00
1.624 " " "	"	"
1.473 " " "	"	"
1.625 " " "	"	"
1.583 " " "	"	"
1.555 " " "	"	"

* N.D. = Not detected at a detection limit of 0.015 mg/cu m.

Discussion

To test the possibility that the chlorinated naphthalenes would not be totally collected as a particulate on a filter (References 3 and 4), the following experiment was performed.

Three 37-mm Type A glass fiber filters were spiked with 270 µg of pentachloronaphthalene using a 24-microliter aliquot of a solution of pentachloronaphthalene in benzene containing 11.2 mg/ml. This represents the amount of pentachloronaphthalene that would be collected at the 2X level in a 270-liter sample. The solvent was allowed to evaporate and 270 liters of air, at a flow rate of approximately 1.5 liters/minute, was pulled through the filters. The filters were then analyzed to determine the amount of pentachloronaphthalene recovered. The results of the experiment are presented below:

µg taken	µg found	Recovery (%)
270	193	71.5
270	198	73.3
270	181	67.0
	mean	70.6

From the above results, it was demonstrated that filter collection is inadequate, because some of the material was volatilized off the filter. The material which vaporized off the filter would have to be collected on either a solid sorbent (i.e., charcoal) or in an organic solvent (in a midget bubbler).

Since pentachloronaphthalene is generated from an organic solvent, the high concentrations of organic solvent vapor could prevent efficient collection of the pentachloronaphthalene vapor on charcoal. To minimize the number of sampling items to be carried by the worker, it was decided to test the possibility of collecting the pentachloronaphthalene vapor and particulate entirely using a midget impinger containing 15 ml of iso-octane.

The collection efficiency of the impinger was tested as follows. Test atmospheres of pentachloronaphthalene were generated by the aspiration/spray-dry technique previously described at a concentration of approximately 2 mg/cu m. Sampling was done with a set of six impingers, each of which was connected in series to a backup impinger. Each impinger was filled with 15 ml of iso-octane which is the maximum volume for sampling at 1.5 liters/minute, and a 270-liter sample was collected over a period of three hours. The contents of each impinger was analyzed by gas chromatography using an electrolytic conductivity detector. The results are presented below:

First Impinger (mg/cu m)	Second Impinger (mg/cu m)
1.241	0.523
1.312	0.446
1.514	0.485
1.575	0.487
1.395	0.482
1.545	0.593

The collection efficiency for the single midget impinger was poor. The midget impinger used in this experiment was designed to collect particles in the respirable size range at a flow rate of 2.8 liters/minute. A flow rate of 1.5 liters/minute is inadequate to collect particles efficiently (> 95%). (Reference No. 5). This occurs because the velocity at the bubbler jet, using a flow rate of 1.5 liters/minute is insufficient to cause impaction and collection of all the particles in the respirable range.

It is therefore necessary to collect pentachloronaphthalene particulate on a glass fiber filter and the vapor, which is not collected on the filter, in a midget bubbler containing 15 ml of iso-octane. Glass fiber filters are used rather than MCEF since the backup pad required to support the MCEF was found to absorb some of the vapor when this method was tested for a similar material (Reference No. 6).

Precision and Accuracy

The statistical procedures used are described in Reference No. 7.

$\overline{CV}_1 = 0.024$ $\overline{CV}_2 = 0.044$ $\overline{CV}_T = 0.067$

Data Sheet: Pentachloronaphthalene S96

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
67.2	68.1	1.013	134.5	131.6	0.978	268.9	263.4	0.980
67.2	65.1	0.969	134.5	137.6	1.023	268.9	269.8	1.003
67.2	67.6	1.006	134.5	136.6	1.016	268.9	255.1	0.949
67.2	69.6	1.036	134.5	130.1	0.967	268.9	263.6	0.980
67.2	68.5	1.019	134.5	138.3	1.028	268.9	266.2	0.990
67.2	68.7	1.022	134.5	133.3	0.991	268.9	273.8	1.018

n =	6	6	6
mean	1.011	1.000	0.987
std dev	0.023	0.025	0.024
CV_1	0.023	0.025	0.024

$\overline{CV}_1$ 0.024

$\overline{CV}_{A+\overline{AMR}}$ 0.026

Based on the above results, no correction for Analytical Method Recovery (A.M.R.) is necessary.

Data Sheet: Pentachloronaphthalene S96

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	73.4	243.2	0.302
	74.7	249.2	0.300
	78.2	257.3	0.304
	72.9	259.3	0.281
	64.6	229.1	0.282
	75.4	259.3	0.291
		n = 6	
		mean	0.293
		std dev	0.010
		CV_2	0.034
1S	163.5	257.3	0.635
	158.6	245.2	0.647
	170.2	251.2	0.678
	162.8	249.2	0.653
	164.4	249.2	0.660
	163.2	261.3	0.625
		n = 6	
		mean	0.650
		std dev	0.019
		CV_2	0.029
2S	290	209.0	1.388
	408	251.2	1.624
	373	253.3	1.473
	392	241.2	1.625
	401	253.3	1.583
	372	239.2	1.555
		n = 6	
		mean	1.541
		std dev	0.094
$\overline{CV}_2$ 0.044		CV_2	0.061

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 8.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Murray, J., Pottie, R., and Pupp, C., Canadian Journal of Chemistry, Vol. 52 (1974).

4. Pupp, C., Lao, R., Murray, J., and Pottie, R., Atmospheric Environment, Vol. 8, Pergamon Press (1974) 915-925.

5. Roberts, L., and McKee, H., Journal of Air Pollution, Vol. 9, No. 1, (May 1959).

6. Failure Report, Chlorodiphenyl, 42%, No. S120, prepared under NIOSH Contract CDC-99-74-45.

7. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

8. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Octachloronaphthalene, No. S97

OSHA Standard: 0.1 mg/cu m

Chemical used for validation: Halowax 1051, Lot B37, Koppers Co.

Procedure

The general procedure used is described in NIOSH Method No. S97 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 30-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in hexane was added to 37 mm Type AA Millipore filters. The analyte was extracted from the filter with hexane and analyzed in a Varian 2700 Gas Chromatograph with a Sc^3H electron capture detector and an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. All data are based on an internal standard approach using 9,10-dichloroanthracene as internal standard. The six samples of each of the 0.5, 1 and 2 times the standard concentration were collected simultaneously. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S97 and in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 was modified to suit the needs for this particular analysis. Hexane was used to extract the samples because it is compatible with the electron capture detector. The amount of solvent used for extraction was increased to 10.0 ml and the sample size analyzed was decreased to 2 µl as a safeguard against working beyond the narrow linear range of the electron capture detector used for the analysis.

Generation

The Aerosol Generation/Dilution System described in the attached section was used for octachloronaphthalene. To generate the octachloronaphthalene particulates, a cooled solution (ice bath at ca. 2°C) of the octachloronaphthalene in xylene was atomized using the ERC Fluid Atomization Aerosol Generator Model 7330.

Initial studies were conducted to determine the concentration of octachloronaphthalene in xylene required to generate the target concentration of 0.20 mg/cu m at 2X the standard level. Experiments were conducted by collecting 3 filter samples (30 liters) at each of the three concentration levels (0.5, 1 and 2X the standard level) generated by atomizing cooled octachloronaphthalene solutions whose concentrations were 0.250, 0.504 and 1.013 g/liter. A semi-logarithmic plot of the data obtained indicated

that a solution containing 0.40 g/liter should be used for the generation of the target concentration. The mean particle size for the aerosols generated in this manner is believed to be in the submicron range.

For the data reported, the test atmosphere samples were generated at 4X the OSHA standard level by atomization of a cooled octachloronaphthalene solution containing 0.397 g/liter into a dry, solvent-free air stream. The atomizer flow rate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The three sample lines were maintained at dilution ratios of 0.106, 0.233, and 0.503 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the three test levels were collected simultaneously at 1.5 liters per minute for 20 minutes (30 liters). Since collection efficiency was found to be 1.00 $\pm$ 0.01, the concentration in the generator and the "found" concentration were considered to be equal.

Collection Efficiency

To determine the collection efficiency of the 37-mm Type AA Millipore filter for octachloronaphthalene aerosols, two filters were mounted back to back in contact with each other and supported by the cellulose backup pad in the filter cassette holder. Six such sample filter cassettes were used to determine the collection efficiency for an air sample concentration of 0.228 mg/cu m at a sampling rate of 1.5 liters per minute for 40 minutes. Each filter was analyzed separately and the relative amount of octachloronaphthalene collected in the primary and backup filters was determined, based on the total quantity found in both filters. The data summarized in Table 1 shows that the average collection efficiency for octachloronaphthalene is 99.9%. Note that two data points have been excluded because of probable contamination of the second filter. Since a solution of octachloronaphthalene in xylene was used in the generation system, any physical wetting of the primary filter with the xylene may cause solution transfer from the primary to the backup filter. This observation appears to be supported by subsequent data on hexachloronaphthalene as described in the Hexachloronaphthalene S100 Backup Data Report, where the efficiency studies were done with separated filters.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0535 \qquad \overline{CV}_2 = 0.0395 \qquad \overline{CV}_T = 0.0674$$

Reference

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE I

Collection Efficiency: Octachloronaphthalene S97

Test Concentration	µg Found on Filter First	Second	Total	% in Second
0.228 mg/cu m	5.95	0.69*	6.640	10.4*
	13.43	0.003	13.433	0.022
	10.75	0.86*	11.610	7.4*
	12.95	0.017	12.967	0.131
	14.25	0.017	14.267	0.119
	14.58	0.004	14.584	0.027
Average.				0.075

Collection Efficiency = 100.0 - 0.08 = 99.92%

* These values were excluded because the second filters were probably contaminated. For these studies the two filters were mounted back to back and in contact with each other.

Data Sheet: Octachloronaphthalene S97

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
1.518	1.732	114.1	3.04	3.13	103.0	6.07	5.97	98.4
1.518	1.355	89.3	3.04	3.09	101.6	6.07	5.93	97.7
1.518	1.422	93.7	3.04	3.05	100.3	6.07	6.13	101.0
1.518	1.424	93.8	3.04	3.04	100.0	6.07	6.13	101.0
1.518	1.543	101.6	3.04	3.00	98.7	6.07	5.88	96.9
1.518	1.503	99.0	3.04	2.99	98.4	6.07	6.16	101.5
n =		6			6			6
mean		98.6			101.3			99.4
std dev		8.752			1.745			1.983
CV_1		0.0888			0.0174			0.0200

$\overline{CV_1}$ 0.0535

$\overline{CV_{A+DE}}$ 0.0578

Data Sheet: Octachloronaphthalene S97

Sampling and Analysis

Test Level	Found			
	µg	Liters		µg/ℓ or mg/cu m
0.5S	1.588	30.17		0.0526
	1.620	30.11		0.0538
	1.545	29.85		0.0518
	1.727	30.09		0.0574
	1.689	30.19		0.0559
	1.694	30.09		0.0563
			n = 6	
			mean	0.0546
			std dev	0.00223
			CV_2	0.0409
1S	3.21	29.99		0.107
	3.17	30.09		0.105
	3.08	29.97		0.103
	3.24	30.13		0.108
	3.36	30.05		0.112
	3.23	30.13		0.107
			n = 6	
			mean	0.107
			std dev	0.00303
			CV_2	0.0283
2S	6.56	30.29		0.217
	6.68	30.11		0.222
	6.81	30.15		0.226
	6.12	30.25		0.202
	6.12	30.13		0.203
	6.73	30.64		0.220
			n = 6	
			mean	0.215
			std dev	0.0101
			CV_2	0.0471
			$\overline{CV_2}$	0.0395

AEROSOL GENERATION/DILUTION/SAMPLING SYSTEM

The aerosol dilution and sampling system is shown schematically in Figure 1. Basically the system consists of a main horizontal line into which aerosol and dilution air are introduced and three vertical dilution and sampling sections which branch off the main line. Figure 2 shows the latter sections in more detail.

Aerosol dilution ratios in the system are fixed by the action of critical flow orifices. Usually an aerosol with a concentration twice the OSHA standard is prepared in the mainline, and this aerosol sampled without dilution in one dilution/sampling section and diluted twofold and fourfold in the other two sections. Other dilution modes may be accommodated simply by changing the critical orifices. There are six sample ports on each section. There is a luer fitting on each sample port to mate with a Millipore filter cassette. Sampling flowrates are controlled by six critical orifices located on each sample manifold.

A number of different aerosol generators including a pneumatic atomizer, an ultrasonic nebulizer, and a dust disperser may be used in conjunction with the dilution and sampling system.

Aerosol Generation

The following aerosol generation equipment is available for use with the system:

- Environmental Research Corporation Fluid Atomization Aerosol Generator Model 7330
- DeVilbiss Model 35A Ultrasonic Nebulizer
- Royco Model WA Aerosol Generator
- Wright Dust Feeder

The ERC and DeVilbiss generators are used to produce aerosols by spray drying or by atomization of suspended solid particles. For spray drying, the material to be dispersed is dissolved in an appropriate solvent, the solution atomized, and the resulting mist mixed with solvent-free air. The solvent evaporates and leaves the nonvolatile solute behind as a residue. Either solid or liquid solutes may be used. Aerosols with median diameters in the 0.03 to 0.5 micron particle size range may be prepared by spray drying with the ERC atomizer. Slightly larger particles may be prepared by spray drying from the DeVilbiss unit. Both aerosol concentration and particle size are functions of the concentration of solute in the atomized solution.

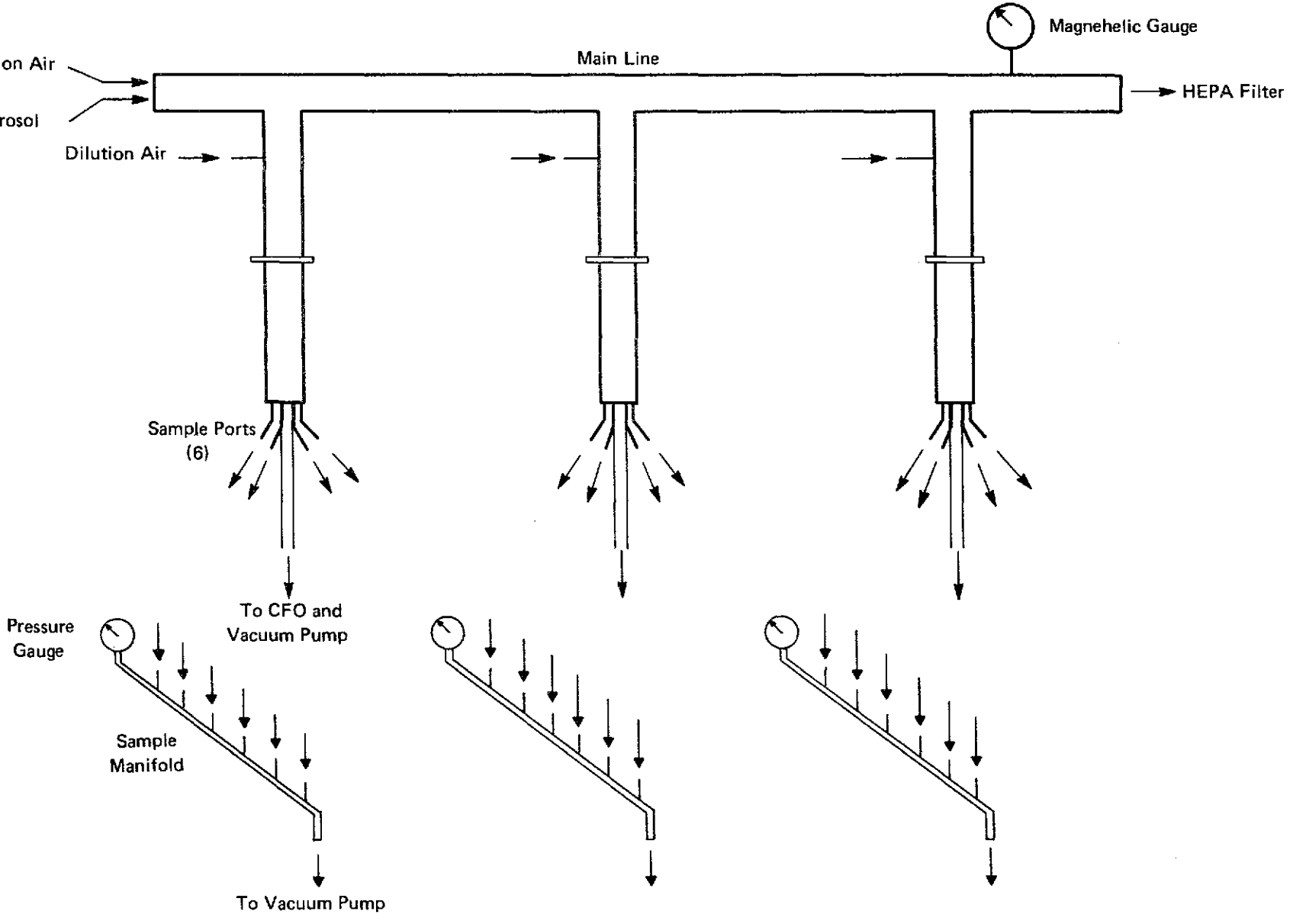

FIGURE 1 AEROSOL DILUTION AND SAMPLING SYSTEM

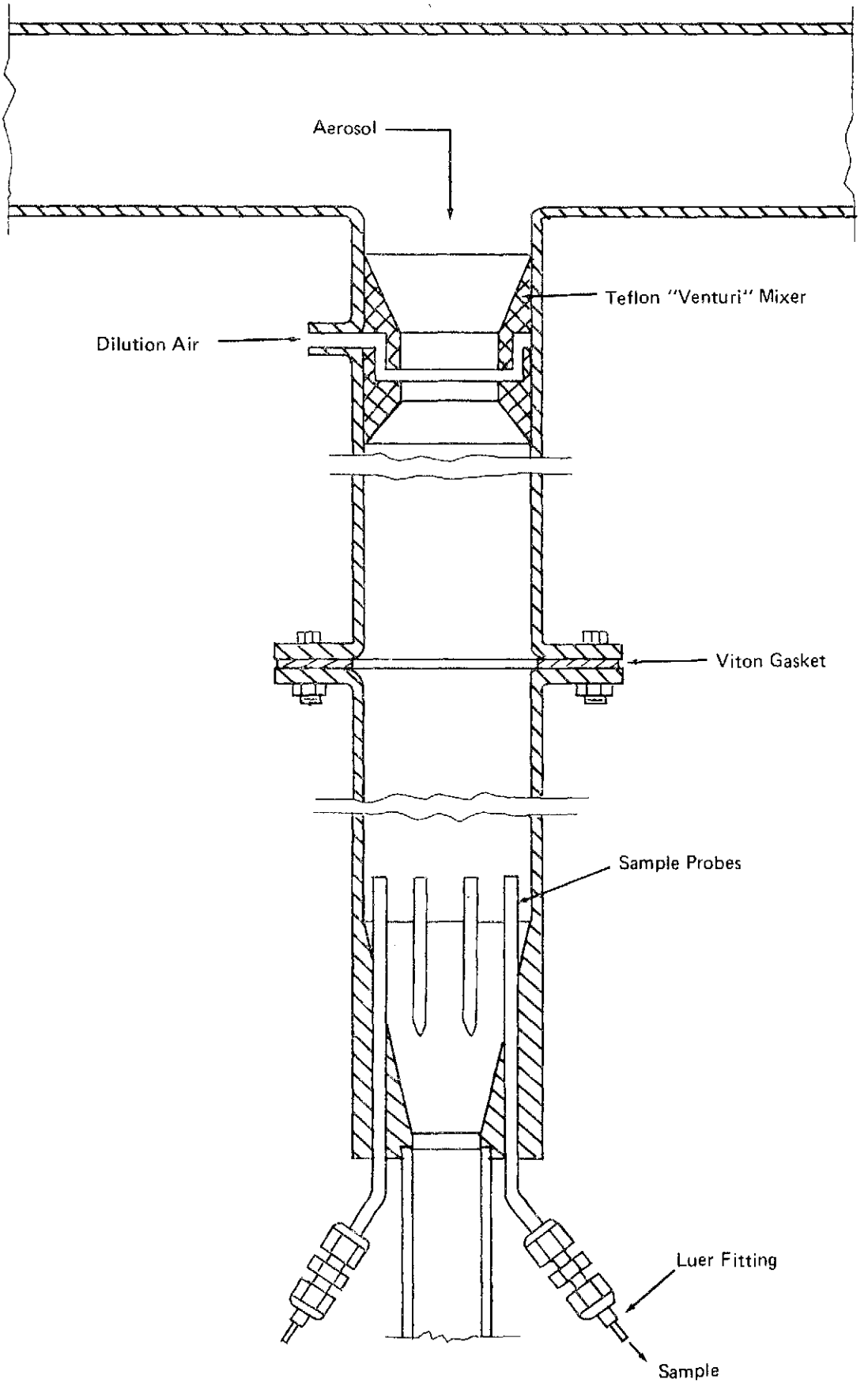

FIGURE 2 CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION
S97-8

Aerosols of solid particles may also be prepared by suspending the particles in a solvent, atomizing the solution and vaporizing the solvent. Solid suspensions with particles up to several microns in diameter may be dispersed with the ERC and DeVilbiss atomizers.

The Royco generator is used primarily to atomize pure liquids. It was designed specifically for atomizing organic liquids such as dioctyl phthalate, and produces DOP aerosol with a median diameter of between 0.5 and 1.0 micron.

The Wright Dust Feeder is used to disperse powders. Samples to be dispersed in the apparatus are compressed into a special holder. In operation, the holder and the dust compact are slowly rotated and driven against a stationary scraper blade which continuously removes dust from the compact surface at a uniform rate. The rate of dust delivery from the feeder may be varied by changing gears in the compact advance mechanism. The powder is entrained in an air stream and is dispersed by impaction on a metal plate. Ideally the size distribution of the particles in the dust cloud should be governed by the particle size distribution of the original powder, however, in practice it is usually difficult to disperse a powder completely. Agglomerates are often formed.

Air Supply

Air from the house compressed air system is treated by successive passage through a cotton filter, a silica gel bed, a high efficiency glass fiber filter, and a membrane filter. These remove respectively, oil and water droplets, water vapor, and fine particles.

The treated air then passes to two parallel air supply manifolds, each of which is equipped with valves for controlling air flow to various parts of the generation/dilution system. One of the manifolds supplies air to the dilution system. The second supplies air to the aerosol generator, either directly or through calibrated rotameters as may be required by the particular generator being used. Pressure in each manifold is maintained at a fixed level by Moore Nullmatic pressure regulators and is measured with bourdon gauges (6" Ashcroft test gauges).

Dilution and Sampling Sections

Aerosol dilution occurs in the Teflon venturi-shaped inserts shown in Figure 2. Dilution air is injected radially into the venturi throat. The quantity of dilution air introduced is fixed by a critical orifice which is connected to one of the constant pressure air manifolds.

Six isokinetic sampling probes are located approximately thirty centimeters downstream of each diluter. The probes convey aerosol to sample collectors (filter cassettes) mounted radially around the outside

of the sampling section. Sample flowrate is fixed at 1.5 liters per minute by critical orifices (sapphire orifices supplied by Richard H. Bird and Co., Waltham, Mass.) mounted on the sample manifold (Figure 1).

As is indicated in Figure 1, a critical orifice is located downstream from the sample probes in each dilution/sampling branch. This orifice is protected from contamination by a Filterite high efficiency filter. There are seven outwardly flowing streams in each branch--one stream is that which flows through the orifice mentioned above (flowrate Q_T) and the other six are the sample streams (total flowrate Q_S). There are two inflowing streams--the dilution air stream (flowrate Q_D) and the aerosol stream entering from the main line (flowrate Q_A). The dilution ratio, R, in each branch is given by:

$$\frac{Q_A}{Q_A + Q_D}$$

or since $Q_T + Q_S = Q_D + Q_A$ (with the assumption of uniform pressure and temperature in the system),

$$R = \frac{Q_T + Q_S = Q_D}{Q_T + Q_S}$$

The flowrates, Q_T, Q_S and Q_D are controlled by the action of critical orifices; consequently the dilution ratios are fixed solely to flow through the critical orifices.

Dilution ratios are measured by adding a small quantity of hydrocarbon gas to the main line and measuring the relative concentrations in each of the three sampling sections using a Beckman 402 hydrocarbon analyzer. Dilution ratios of 1.00 to 0.488 to 0.241 are typical when the system is set to generate a 2X OSHA standard concentration in the main line. No measurable differences (within 1%) in the hydrocarbon concentration were found among the six sample ports on any of the three sampling ports. The dilution ratios are rechecked periodically.

The main line flowrate is about 150 liters per minute when a 2X OSHA standard concentration is being generated in the main line. Flow through the dilution/sampling branches is approximately 70 liters per minute.

Excess aerosol from the main line is passed through a HEPA filter and then vented to a hood.

Experimental Procedure

1) The aerosol generator parameters necessary to produce the desired aerosol concentration are found by making several trial runs. If the

spray drying procedure is being used, the concentration of the atomizer solution would be varied in the trial runs. If the dust feeder were being used, the sample feed rate would be varied.

2) Six samples, each consisting of two filters sampling in series are taken from the 2X OSHA standard sampling ports to verify that the collection efficiency of the filters is adequate.

3) A full set of eighteen samples are collected simultaneously.

Typical System Parameters

When the dilution/sampling system is set up to produce aerosols with a 2X OSHA standard concentration in the main line, typical values of the system parameters are:

Main line pressure:	+ 3 cm H_2O with respect to atmospheric pressure
Main line flowrate:	150 liters per minute
Sampling rate:	1.5 liters per minute
Flowrate through dilution/ sampling branch (approximate):	68 liters per minute

Dilution air flowrate (approximate):

2X OSHA standard branch	0
1X OSHA standard branch	36
0.5X OSHA standard branch	53

Dilution ratios (measured with hydrocarbon analyzer):	1.00:0.488:0.241

BACKUP DATA REPORT

Substance:	Methyl Iodide, No. S98
OSHA Standard:	5 ppm (28 mg/cu m)
Chemical used for validation:	Methyl Iodide, Certified Gas Mixture Matheson Gas Products Iodomethame, 99% Chemical Samples Co.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of methyl iodide in air is described in NIOSH Method S98, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 350 mg/ml solution of methyl iodide in toluene injected with a 10-µl syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 50-liter air sample at the respective level. The eluting solvent was toluene.

Samples of methyl iodide in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of methyl iodide in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 50 minutes). The "true" concentrations of methyl iodide in the generated samples were determined by gas chromatographic analysis using a 5-ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of methyl iodide. Details of the analytical procedures are given in the Analytical Procedures Section of Reference 1.

Modifications

The P&CAM 127 method was used with one modification. Chromosorb 101, FFAP and Poropak Q were tried as column packings. Chromosorb 101 and FFAP did not separate carbon disulfide and methyl iodide. Poropak Q was considered unsatisfactory because the retention time for carbon disulfide was about 30 minutes. Chromosorb 101 was satisfactory when toluene was used as the eluting solvent. However, overnight desorption (at least 8 hrs) is required to obtain complete desorption.

Generation

A gas mixture of methyl iodide in nitrogen at twice the OSHA standard level was purchased from Matheson Gas Products. The

concentration was verified by gas chromatographic analysis using bag samples for comparison. These were prepared in 4-liter Teflon® bags as described above. The test atmosphere was generated by directly sampling the mixture. The 3 concentrations were obtained by sampling only at the first stage and repeating the generation with appropriate dilution with nitrogen for concentrations 0.5 and 1 times the OSHA standard level. Complete mixing was assured by passing the stream of analyte through 2 mixers before sampling. The total gas flow rate was 2, 4, and 8 ℓ/min for 0.5, 1, and 2 times the OSHA standard respectively. Sampling time was 50 minutes with a nominal flow rate of 1 ℓ/min for each charcoal tube. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation Section of Reference 2.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 52 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration had reached only 2 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 12.5 mg of methyl iodide and at the recommended sampling rate, the breakthrough volume is greater than 240 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.043 \qquad \overline{CV}_2 = 0.045 \qquad \overline{CV}_T = 0.070$$

The average recovery of the generated samples over all levels was:

90.0%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Methyl Iodide

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.700	0.608	0.868	1.400	1.234	0.882	2.800	2.494	0.891
0.700	0.620	0.885	1.400	1.278	0.913	2.800	2.607	0.931
0.700	0.623	0.890	1.400	1.270	0.907	2.800	2.589	0.925
0.700	0.578	0.826	1.400	1.280	0.914	2.800	2.562	0.915
0.700	0.626	0.895	1.400	1.289	0.921	2.800	2.623	0.937
0.700	0.517	0.739	1.400	1.271	0.908	2.800	2.609	0.932
n =		6			6			6
mean		0.851			0.907			0.922
std dev		0.0601			0.0135			0.0169
CV_1		0.0706			0.0149			0.0184

CV_1 0.0430

$\overline{CV}_{A+\overline{DE}}$ 0.0464

Data Sheet: Methyl Iodide S98

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.743	0.867	56.0	15.476	17.0	91.0
	0.733	0.859	53.0	16.210	17.0	95.4
	0.687	0.799	52.0	15.371	17.0	90.4
	0.726	0.852	54.5	15.634	17.0	92.0
	0.695	0.810	51.5	15.723	17.0	92.5
	0.619	0.729	51.0	14.296	17.0	84.1
			n = 6			
			mean	15.452		90.9
			std dev	0.636		
			CV_2	0.041		
1S	1.290	1.435	56.0	25.626	29.0	88.4
	1.239	1.380	53.0	26.032	29.0	89.8
	1.235	1.384	52.0	26.609	29.0	91.8
	1.223	1.361	54.5	24.980	29.0	86.1
	1.234	1.380	51.5	26.792	29.0	92.4
	1.324	1.477	51.0	28.957	29.0	99.9
			n = 6			
			mean	26.499		91.4
			std dev	1.373		
			CV_2	0.052		
2S	2.210	2.408	56.0	43.007	52.0	82.7
	2.181	2.378	53.0	44.875	52.0	86.3
	2.119	2.310	52.0	44.414	52.0	85.4
	2.318	2.525	54.5	46.335	52.0	89.1
	2.207	2.405	51.5	46.691	52.0	89.8
	2.247	2.452	51.0	48.079	52.0	92.5
			n = 6			
			mean	45.567		87.6
			std dev	1.818		
			CV_2	0.040	$\overline{CV}_2$	0.045

* All values have passed the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

Backup Data Report

Substance: Hexachloronaphthalene, No. S100

OSHA Standard: 0.2 mg/cu m

Chemical used for validation: Halowax 1014, Lot B77, Koppers Co.

Procedure

The general procedure used is described in NIOSH Method No. S97 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 30-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in hexane was added to 37 mm Type AA Millipore filters. The analyte was extracted from the filter with hexane and analyzed in a Varian 2700 Gas Chromatograph with a Sc ^{3}H electron capture detector and an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. All data are based on an internal standard approach using 1, 4, bis-hexachloroxylene as internal standard. The six samples of each of the 0.5, 1 and 2 times the standard concentration were collected simultaneously. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S100 and in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM was modified to suit the needs for this particular analysis. Hexane was used to extract the samples because it is compatible with the electron capture detector. The amount of solvent used for extraction was increased to 10.0 ml and the sample size analyzed was decreased to 2 µl as a safeguard against working beyond the narrow linear range of the electron capture detector used for the analysis.

Generation

Test atmosphere samples at a concentration 4X the OSHA standard level were generated by atomization of a cooled hexachloronaphthalene solution in xylene containing 0.999 g/liter into a dry solvent-free air stream flow The atomizer flowrate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry solvent-free air. The three sample lines were maintained at dilution ratios of 0.106, 0.233, and 0.503 to produce the 0.5, 1, and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 20 minutes (30 liters). Since collection efficiency was found to be 1.00 ± 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate hexachloronaphthalene was determined by collecting six filter samples at air sample concentrations of 0.56, 0.85, and 0.33 mg/cu m. The physical layout of the filter series used for collection was slightly modified for each of the three sets of 6 samples collected in order to determine the probable effect of "solution transfer" of hexachloronaphthalene to other surfaces in contact with the front filter. For Experiment A, the two filters were mounted back to back in contact with each other and supported by the backup pad; for Experiment B, two separate filter cassettes (each with filter and backup pad) were used; for Experiment C, a single three-piece filter cassette was used whereby Filter 1 was mounted in grooves above the standard filter and backup pad arrangement (Filter 1 was not in contact with any filter or backup pad). The data shown in Table 1 for Experiments A and B indicates that some transfer of hexachloronaphthalene to other surfaces in contact with the filter does occur; 6.6% was found on the second filter in contact with the first filter and 5.9% was found on the backup pad also in contact with the first filter. This observation is probably unique to the manner in which we were generating the hexachloronaphthalene and is due to xylene solution transport. Field collection of samples should be done using the standard aerosol field monitors.

The Experiment C data shows that the filter collection efficiency for hexachloronaphthalene is 98.9%.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0577 \qquad \overline{CV}_2 = 0.0292 \qquad \overline{CV}_T = 0.0626$$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Hexachloronaphthalene Collection Efficiency

Test Concentration	µg Found			% Found
	Filter 1	Filter 2	Total	Filter 2
Experiment A:				
0.56 mg/cu m	22.8	1.85	24.65	7.5
	27.5	2.34	29.84	7.8
	18.8	1.13	19.93	5.7
	24.0	1.26	25.26	5.0
	18.4	1.35	19.75	6.8
	30.0	2.25	32.25	7.0
Average				6.6

	µg Found				% Found	
	Filter 1	Back-Up Pad	Filter 2	Total	Back-Up Pad	Filter 2
Experiment B:						
0.85 mg/cu m	33.0	1.94	0.04	34.98	5.5	0.11
	37.5	2.25	0.04	39.79	5.7	0.10
	39.5	2.07	0.09	41.66	5.0	0.22
	33.0	2.12	0.18	35.30	6.0	0.50
	37.0	2.25	0.14	39.39	5.7	0.34
	35.0	2.79	0.18	37.97	7.3	0.47
Average					5.9	0.29

	µg Found			% Found
	Filter 1	Filter 2	Total	Filter 2
Experiment C:				
0.33 mg/cu m	13.56	0.13	13.69	0.95
	14.73	0.16	14.89	1.07
	15.36	0.11	15.47	0.71
	15.01	0.14	15.15	0.92
	14.60	0.24	14.84	1.62
	16.30	0.19	16.49	1.15
Average				1.07

Collection Efficiency = 100.0 - 1.1 = 98.9%

Experiment A - one cassette with two filters back to back.

Experiment B - two filter cassettes in series.

Experiment C - one cassette with two non-touching filters in series.

Data Sheet: Hexachloronaphthalene, S100

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
2.97	2.72	91.6	5.94	6.03	101.5	11.88	11.54	97.1
2.97	3.00	101.0	5.94	6.22	104.7	11.88	11.70	98.5
2.97	2.91	98.0	5.94	5.86	98.7	11.88	11.22	94.4
2.97	2.67	89.9	5.94	5.91	99.5	11.88	11.15	93.9
2.97	3.40	114.5	5.94	6.21	104.5	11.88	11.38	95.8
2.97	2.96	99.7	5.94	5.62	94.6	11.88	11.99	100.9
n =		6			6			6
mean		99.1			100.6			96.8
std dev		8.76			3.84			2.64
CV_1		0.0883			0.0382			0.0273

$\overline{CV}_1$ 0.0577

$\overline{CV}_{A+\overline{DE}}$ 0.0624

Data Sheet: Hexachloronaphthalene, S100

Sampling and Analysis

Test Level	Found µg	Found Liters		µg/ℓ or mg/cu m
0.5S	3.04	30.1		0.101
	3.31	30.0		0.110
	3.09	29.8		0.104
	3.09	30.0		0.103
	3.05	30.1		0.101
	3.12	30.0		0.104
			n = 6	
			mean	0.104
			std dev	0.0033
			CV_2	0.0318
1S	6.38	29.9		0.213
	6.46	30.0		0.215
	6.21	29.9		0.208
	6.07	30.1		0.202
	6.65	30.0		0.222
	6.20	30.1		0.206
			n = 6	
			mean	0.211
			std dev	0.0072
			CV_2	0.0339
2S	13.95	30.2		0.462
	13.50	30.0		0.450
	14.18	30.1		0.471
	13.75	30.2		0.455
	14.06	30.1		0.467
	13.75	30.6		0.449
			n = 6	
			mean	0.459
			std dev	0.0091
			CV_2	0.0198
			$\overline{CV_2}$	0.0292

BACKUP DATA REPORT

Substance:	Hexachloroethane, No. S101
OSHA Standard:	1 ppm (10 mg/cu m)
Chemical used for validation:	Hexachloroethane Matheson Coleman & Bell

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of hexachloroethane in air is described in NIOSH Method S101, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 12.5 mg/ml solution of hexachloroethane in carbon tetrachloride injected with a syringe. Carbon tetrachloride was used because hexachloroethane is not sufficiently soluble in carbon disulfide. The amount of solution added was 4, 8, and 16 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 10-liter air sample at the respective level. The eluting solvent was carbon disulfide. Samples of hexachloroethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of hexachloroethane in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 50 minutes). The "true" concentrations of hexachloroethane in the generated samples were determined by gas chromatographic analysis using a 5-ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, gollowed by injecting the required amount of hexachloroethane solution. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two major modifications. An internal standard was used for improved accuracy. A glass column was used to avoid extra peaks observed while using a stainless steel column.

Generation

The test atmosphere was generated by a vapor saturation technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2, nitrogen flow through

the saturator was 74 ml/min. The total gas flow rate of the first stage was 23.1 liters per minute. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube. Concentrations calculated from air flow and nitrogen flow through the saturator agreed with gas chromatographic analysis of the diluted atmosphere within less than 5 percent.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 23.4 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration was less than 5% of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 1.1 mg of hexachloroethane and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.014 \qquad \overline{CV}_2 = 0.110 \qquad \overline{CV}_T = 0.121$$

The average recovery of the generated samples over all levels was:

93.3%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Hexachloroethane S101

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.050	0.049	0.987	0.100	0.099	0.986	0.200	0.195	0.974
0.050	0.049	0.987	0.100	0.097	0.975	0.200	0.196	0.978
0.050	0.049	0.989	0.100	0.099	0.992	0.200	0.195	0.975
0.050	0.049	0.980	0.100	0.101	1.007	0.200	0.198	0.988
0.050	0.048	0.952	0.100	0.102	1.018	0.200	0.192	0.962
0.050	0.049	0.985	0.100	0.101	1.010	0.200	0.194	0.969
n =		6			6			6
mean		0.980			0.998			0.974
std dev		0.0140			0.0163			0.0087
CV_1		0.0143			0.0163			0.0090

CV_1 0.0136

$\overline{CV}_{A+\overline{DE}}$ 0.0147

Data Sheet: Hexachloroethane S101

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.0555	0.0563	9.60	5.86	5.50	106.6
	0.0560	0.0567	9.60	5.91	5.50	107.4
	0.0388	0.0403	9.25	4.35	5.50	79.1
	0.0503	0.0513	9.60	5.34	5.50	97.1
	0.0384	0.0398	8.90	4.47	5.50	81.3
	0.0531	0.0540	9.40	5.74	5.50	104.4
			n = 6			
			mean	5.279		96.0
			std dev	0.702		
			CV_2	0.130		
1S	0.0937	0.0939	9.15	10.26	10.60	96.8
	0.1032	0.1035	10.25	10.10	10.60	95.3
	0.0963	0.0965	10.05	9.60	10.60	90.6
	0.1041	0.1044	9.10	11.48	10.60	108.2
	0.1101	0.1105	9.55	11.56	10.60	109.1
	0.0799	0.0801	9.10	8.80	10.60	83.1
			n = 6			
			mean	10.302		97.2
			std dev	1.071		
			CV_2	0.104		
2S	0.2519	0.2637	10.85	24.30	25.00	97.2
	0.1827	0.1867	9.70	19.25	25.00	77.0
	0.1798	0.1836	9.40	19.53	25.00	78.1
	0.1992	0.2047	9.30	22.00	25.00	88.0
	0.2178	0.2252	10.15	22.19	25.00	88.8
	0.2175	0.2249	9.85	22.83	25.00	91.3
			n = 6			
			mean	21.684		86.7
			std dev	1.956		
			CV_2	0.0902	$\overline{CV}_2$	0.110

BACKUP DATA REPORT

Substance: Ethylene Chlorohydrin, No. S103

OSHA Standard: 5 ppm (16 mg/cu m)

Chemical used for validation: 2-Chloroethanol, 99% Chemical Samples Co.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of ethylene chlorohydrin in air is described in NIOSH Method S103, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with an 80 mg/ml solution of ethylene chlorohydrin in isopropyl alcohol injected with a 10-µl syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 20-liter air sample at the respective level. The eluting solvent was carbon disulfide containing 5% isopropanol.

Samples of ethylene chlorohydrin in air were generated and collected on petroleum-derived activated Lot 104, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of ethylene chlorohydrin in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 100 minutes). The "true" concentrations of ethylene chlorohydrin in the generated samples were determined by gas chromatographic analysis using a 5-ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of ethylene chlorohydrin. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with two major modifications. Lot 104 charcoal was used as absorbant. A mixed solvent of 5% isopropyl alcohol in carbon disulfide was used as the eluting solvent. These modifications were made to improve desorption efficiency. (See the Discussion Section for further explanation.)

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of

the atmosphere generation equipment and operations are presented in the Atmosphere Generation section Reference 2. The total gas flow rate of the first stage was 22.2 liters per minute, and the rate of ethylene chlorohydrin injection was 0.0419 g/hr. Sampling time was 100 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 31.49 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration was less than 5% of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 1.5 mg of ethylene chlorohydrin and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Discussion

Desorption efficiency tests for ethylene chlorohydrin were run using coconut (Lot 105) and petroleum-derived (Lot 104) charcoal from SKC, Inc. Carbon disulfide and carbon disulfide containing 5% isopropyl alcohol were used as desorbing solvents. The results are summarized in Table 1.

TABLE 1. DESORPTION EFFICIENCY AT 1X OSHA STANDARD

mg Taken	mg Found*	D.E.*	Charcoal	Solvent
0.3200	0.0637	0.199	Lot 105	Carbon Disulfide
0.3200	0.1522	0.475	Lot 104	Carbon Disulfide
0.3200	0.2993	0.935	Lot 104	5% Isopropanol in Carbon Disulfide

* The average value of six samples.

From these results, petroleum-derived charcoal using 5% isopropanol in carbon disulfide was chosen for this method.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.052 \qquad \overline{CV}_2 = 0.054 \qquad \overline{CV}_T = 0.076$$

The average recovery of the generated samples over all levels was:

91.4%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Ethylene Chlorohydrin S103

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.160	0.133	0.834	0.320	0.307	0.960	0.640	0.597	0.932
0.160	0.145	0.908	0.320	0.285	0.889	0.640	0.601	0.940
0.160	0.147	0.921	0.320	0.318	0.994	0.640	0.599	0.935
0.160	0.152	0.949	0.320	0.283	0.886	0.640	0.594	0.928
0.160	0.142	0.889	0.320	0.301	0.940	0.640	0.692	1.081
0.160	0.150	0.940	0.320	0.302	0.944	0.640	0.642	1.003
n =		6			6			6
mean		0.907			0.936			0.970
std dev		0.0419			0.0419			0.0613
CV_1		0.0462			0.0448			0.0632

CV_1	0.0521
$\overline{CV}_{A+\overline{DE}}$	0.0562

Data Sheet: Ethylene Chlorohydrin S103

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.1173	0.1229	19.20	6.40	7.31	87.6
	0.1188	0.1247	19.20	6.49	7.31	88.8
	0.0592	0.0517	18.50	2.79*	7.31	38.2*
	0.1173	0.1229	19.20	6.40	7.31	87.6
	0.1258	0.1331	17.80	7.48	7.31	102.3
	0.1173	0.1229	18.80	6.54	7.31	89.4
			n = 5			
			mean	6.66		91.1
			std dev	0.460		
			CV_2	0.069		
1S	0.2572	0.2841	18.30	15.52	15.21	102.1
	0.2577	0.2846	20.50	13.88	15.21	91.3
	0.2477	0.2736	20.10	13.61	15.21	89.5
	0.2257	0.2490	18.20	13.68	15.21	90.0
	0.2593	0.2864	19.10	15.00	15.21	98.6
	0.2353	0.2598	18.20	14.27	15.21	93.8
			n = 6			
			mean	14.33		94.2
			std dev	0.775		
			CV_2	0.054		
2S	0.6157	0.6305	21.70	29.05	31.49	92.3
	0.5120	0.5401	19.40	27.84	31.49	88.4
	0.4701	0.5013	18.80	26.67	31.49	84.7
	0.4089	0.4424	18.60	23.78	31.49	75.5*
	0.5556	0.5791	20.30	28.53	31.49	90.6
	0.5233	0.5503	19.70	27.94	31.49	88.7
			n = 5			
			mean	28.00		88.9
			std dev	0.894		
			CV_2	0.032		

* Deleted as an outlier, because this value did not pass the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

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BACKUP DATA REPORT

Substance:	Ethylene Dibromide S104
OSHA Standard:	230 mg/cu m (Ceiling) 155 mg/cu m (T.W.A.)
Chemical used for validation:	Ethylene Dibromide, reagent grade The Dow Chemical Company

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 55 mg/ml solution of ethylene dibromide in n-heptane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 1-liter air sample at the respective level. The eluting solvent was carbon disulfide. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-pentadecane as internal standard. Details of the anlytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with one modification. An internal standard was added for improved accuracy.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.7 liters per minute, and the rate of ethylene dibromide injection was 0.72 g/hr. Sampling time was 5 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 446 mg/cu m). Breakthrough is defined as the time at which the

effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration had reached only 2 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 21.4 mg of ethylene dibromide and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$\overline{CV_1} = 0.027$ $\overline{CV_2} = 0.058$ $\overline{CV_T} = 0.077$

The average recovery of the generated samples over all levels was:

92.9

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Ethylene Dibromide S104

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.110	0.103	0.940	0.220	0.211	0.957	0.440	0.403	0.916
0.110	0.106	0.960	0.220	0.213	0.967	0.440	0.399	0.907
0.110	0.102	0.928	0.220	0.206	0.935	0.440	0.376	0.855
0.110	0.103	0.934	0.220	0.205	0.932	0.440	0.376	0.854
0.110	0.101	0.916	0.220	0.200	0.908	0.440	0.380	0.864
0.110	0.098	0.890	0.220	0.200	0.908	0.440	0.386	0.878
n =		6			6			6
mean		0.928			0.935			0.879
std dev		0.0235			0.0246			0.0267
CV_1		0.0253			0.0264			0.0304

CV_1 0.0274

$\overline{CV}_{A+\overline{DE}}$ 0.0296

Data Sheet: Ethylene Dibromide S104

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.096	0.103	0.915	112.7	118	95.5
	0.106	0.114	1.025	111.0	118	94.1
	0.092	0.099	1.005	98.5	118	83.5
	0.092	0.099	0.910	108.8	118	92.2
	0.103	0.111	0.955	115.7	118	98.1
	0.099	0.106	0.910	116.2	118	98.4
			n = 6			
			mean	110.5		93.6
			std dev	6.50		
			CV_2	0.0588		
1S	0.221	0.240	1.085	221.0	236	93.7
	0.199	0.215	0.970	221.5	236	93.8
	0.167	0.180	0.940	191.0	236	80.9
	0.181	0.194	0.930	208.6	236	88.4
	0.216	0.234	1.015	230.9	236	97.8
	0.207	0.223	0.985	226.8	236	96.1
			n = 6			
			mean	216.6		91.8
			std dev	14.63		
			CV_2	0.0675		
2S	0.467	0.542	1.085	499.4	506	98.7
	0.414	0.473	0.970	488.0	506	96.5
	0.370	0.417	0.940	444.1	506	87.8
	0.394	0.448	0.930	481.8	506	95.2
	0.406	0.463	1.015	456.1	506	90.1
	0.402	0.458	0.985	465.1	506	91.9
			n = 6			
			mean	472.4		93.4
			std dev	20.9		
			CV_2	0.0442	$\overline{CV}_2$	0.0577

BACKUP DATA REPORT

Substance:	Ethyl Bromide, No. S106
OSHA Standard:	200 ppm (890 mg/cu m)
Chemical used for validation:	Ethyl Bromide, Certified Gas Mixture Matheson Gas Products Ethyl Bromide, Reagent Grade Baker and Adamson

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of ethyl bromide in air is described in NIOSH Method S106, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat ethyl bromide injected with a 10-µl syringe. The amount of solution added was 1.2, 2.5, and 4.9 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 4-liter air sample at the respective level. The eluting solvent was isopropyl alcohol. Samples of ethyl bromide in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of ethyl bromide in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 20 minutes). The "true" concentrations of ethyl bromide in the generated samples were determined by gas chromatographic analysis using a 5 ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of ethyl bromide. Details of the analytical procedures are given in the Analytical Procedures Section of Reference 1.

Modifications

The P&CAM 127 method was used with two modifications. Isopropyl alcohol was used as the eluting solvent and desorption was done overnight. Isopropyl alcohol was used as the eluting solvent because carbon disulfide had the same retention time as ethyl bromide on the gas chromatograph column. Preliminary experiments using isopropyl alcohol to desorb ethyl bromide from charcoal indicated that desorption was not complete in 30 minutes; desorption efficiency increases with overnight desorption.

Generation

A gas mixture of ethyl bromide in nitrogen at twice the OSHA standard level was purchased from Matheson Gas Products. The concentration was verified by gas chromatographic analysis using bag samples for comparison. These were prepared in 4-liter Teflon® bags as described above. The test atmosphere was generated by directly sampling the mixture. The 3 concentrations were obtained by sampling only at the first stage and repeating the generation with appropriate dilution with nitrogen for concentrations 0.5 and 1 times the OSHA standard level. Complete mixing was assured by passing the stream of analyte through 2 mixers before sampling. The total gas flow rate was 2, 4, and 8 ℓ/min for 0.5, 1, and 2 times the OSHA standard respectively. Sampling time was 20 minutes with a nominal flow rate of 200 ml/min for each charcoal tube. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation Section of Reference 2.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 2213 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred at 32 minutes. Thus the capacity of this lot of charcoal is 14.2 mg of ethyl bromide and at the recommended sampling rate, the breakthrough volume is 6.4 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.025 \qquad \overline{CV}_2 = 0.019 \qquad \overline{CV}_T = 0.054$$

The average recovery of the generated samples over all levels was:

93.8%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Ethyl Bromide S106

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
1.780	1.380	0.775	3.560	2.960	0.832	7.120	6.450	0.906
1.780	1.476	0.829	3.560	3.062	0.860	7.120	6.286	0.883
1.780	1.483	0.833	3.560	2.971	0.835	7.120	5.997	0.842
1.780	1.459	0.820	3.560	3.004	0.844	7.120	6.029	0.847
1.780	1.489	0.836	3.560	2.943	0.827	7.120	6.185	0.869
1.780	1.426	0.801	3.560	2.938	0.825	7.120	6.057	0.851
n =		6			6			6
mean		0.816			0.837			0.866
std dev		0.0236			0.0131			0.0247
CV_1		0.0289			0.0156			0.0285

CV_1 0.0251

$\overline{CV}_{A+\overline{DE}}$ 0.0271

Data Sheet: Ethyl Bromide S106

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.519	1.851	3.840	482.1	547	88.1
	1.471	1.793	3.840	466.8	547	85.3
	1.429	1.743	3.700	471.0	547	86.1
	1.535	1.870	3.840	487.0	547	89.0
	1.376	1.678	3.560	471.3	547	86.2
	1.468	1.790	3.760	476.0	547	87.0
			n = 6			
			mean	475.7		87.0
			std dev	7.6		
			CV_2	0.016		
1S	3.098	3.725	3.660	1017.8	1071	95.0
	3.581	4.286	4.100	1045.4	1071	97.6
	3.559	4.258	4.020	1059.2	1071	98.9
	3.249	3.905	3.640	1072.8	1071	100.2
	3.171	3.812	3.820	997.8	1071	93.2
	3.102	3.731	3.640	1025.0	1071	95.7
			n = 6			
			mean	1036.3		96.8
			std dev	27.9		
			CV_2	0.027		
2S	8.188	9.359	4.340	2156.5	2198	98.1
	1.704	2.063	3.880	531.7*	2198	24.2*
	6.930	8.026	3.760	2134.7	2198	97.1
	6.867	7.942	3.720	2135.0	2198	97.1
	7.635	8.767	4.060	2159.5	2198	98.2
	7.349	8.480	3.940	2152.4	2198	97.9
			n = 5			
			mean	2147.6		97.7
			std dev	11.9		
			CV_2	0.006	$\overline{CV}_2$	0.019

* Deleted as an outlier, because this value did not pass the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

BACKUP DATA REPORT

Substance:	Difluorodibromomethane, No. S107
OSHA Standard:	100 ppm (860 mg/cu m)
Chemical used for validation:	Difluorodibromomethane PCR Incorporated Difluorodibromomethane, Certified Gas Mixture Matheson Gas Products

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency, 100 mg samples of charcoal were placed in 2 ml Varian Automatic Sample Injector Vials and were spiked with neat difluorodibromomethane using a 10-µl syringe. The amount added was 7.3, 3.7, and 1.8 µl, respectively for the 2, 1, and 0.5 times the OSHA standard level. This was the amount present in a 10-liter air sample at the respective level. The spiking was done in a cold room because difluorodibromomethane boils at room temperature (B.P. = 24.5°C, d^0 = 2.35). The eluting solvent was isopropyl alcohol. Standards were also prepared in a cold room by injecting difluorodibromomethane with a 10-µl syringe into 2-ml Hewlett Packard Automatic Sample Injector Vials containing isopropyl alcohol.

Samples of difluorodibromomethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of difluorodibromomethane in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 50 minutes). The "true" concentrations of difluorodibromomethane in the generated samples were determined by gas chromatographic analysis using a 5 ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of difluorodibromomethane. Details of the analytical procedures are given in the Analytical Procedures Section of Reference 1.

Modifications

The P&CAM 127 method was used with three modifications. Isopropyl alcohol was used as the eluting solvent and desorption was done overnight. Isopropyl alcohol was used as the eluting solvent because carbon disulfide had the same retention time as

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difluorodibromomethane on the gas chromatograph column. Chromosorb 101 and Poropak Q also did not separate difluorodibromomethane from carbon disulfide. Preliminary experiments using isopropyl alcohol to desorb difluorodibromomethane from charcoal indicated that desorption was not complete in 30 minutes; desorption efficiency increases with overnight desorption. To avoid the problem of migration of the difluorodibromomethane from the sample section to the backup section of a single tube after collection, two large tubes in series were used and separated and capped immediately after sampling.

Generation

A gas mixture of difluorodibromomethane in nitrogen at twice the OSHA standard level was purchased from Matheson Gas Products. The concentration was verified by gas chromatographic analysis using bag samples for comparison. These were prepared in 4-liter Teflon® bags as described above. The test atmosphere was generated by directly sampling the mixture. The 3 concentrations were obtained by sampling only at the first stage and repeating the generation with appropriate dilution with nitrogen for concentrations 0.5 and 1 times the OSHA standard level. Complete mixing was assured by passing the stream of analyte through 2 mixers before sampling. The total gas flow rate was 2, 4, and 8 ℓ/min for 0.5, 1, and 2 times the OSHA standard respectively. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation Section of Reference 2.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 1875 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred at 1 hour, 18 minutes. Thus the capacity of this lot of charcoal is 29.3 mg of difluorodibromomethane and at the recommended sampling rate, the breakthrough volume is 15.6 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.067 \qquad \overline{CV}_2 = 0.070 \qquad \overline{CV}_T = 0.090$$

The average recovery of the generated samples over all levels was:

102.5%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Difluorodibromomethane S107

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
4.40	4.72	1.072	8.94	8.65	0.967	18.53	14.92	0.805
4.40	4.92	1.118	8.94	10.13	1.133	18.53	14.82	0.800
4.40	4.48	1.018	8.94	9.60	1.074	18.53	17.17	0.926
4.40	4.97	1.129	8.94	9.00	1.006	18.53	18.18	0.981
4.40	4.46	1.014	8.94	9.01	1.008	18.53	15.03	0.811
4.40	5.04	1.145	8.94	9.01	1.008	18.53	16.35	0.882
n =		6			6			6
mean		1.083			1.033			0.868
std dev		0.057			0.060			0.075
CV_1		0.053			0.058			0.087

$$\frac{CV_1}{CV_{A+DE}} \quad \begin{matrix} 0.067 \\ 0.073 \end{matrix}$$

Data Sheet: Difluorodibromomethane S107

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	4.851	4.284	9.600	446	470	95.0
	4.851	4.284	9.600	446	470	95.0
	4.564	3.933	9.250	425	470	90.5
	4.766	4.181	9.600	435	470	92.7
	4.293	3.603	8.900	405	470	86.1
	4.716	4.119	9.400	438	470	93.2
			n = 6			
			mean	433		92.1
			std dev	15.8		
			CV_2	0.036		
1S	8.797	9.115	9.150	996	932	106.9
	8.864	9.197	10.250	897	932	96.3
	8.479	8.726	10.050	868	932	93.2
	9.081	9.463	9.100	1040	932	111.6
	9.098	9.483	9.550	993	932	106.5
	9.287	9.639	9.100	1059	932	113.7
			n = 6			
			mean	976		104.7
			std dev	76.8		
			CV_2	0.079		
2S	19.038	21.650	10.850	1995	1876	106.4
	18.048	20.464	9.700	2110	1876	112.5
	18.744	21.253	9.400	2261	1876	120.5
	18.293	20.765	9.300	2233	1876	119.0
	16.143	18.036	10.150	1777	1876	94.7
	18.048	20.464	9.850	2078	1876	110.7
			n = 6			
			mean	2076		110.6
			std dev	176.6		
			CV_2	0.085	$\overline{CV}_2$	0.070

* All values have passed the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

BACKUP DATA REPORT

Substance:	1,2-Dichloroethylene, No. S110
OSHA Standard:	200 ppm (790 mg/cu m)
Chemical used for validation:	1.2-Dichloroethylene, Certified Gas Mixture Matheson Gas Products

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,2-dichloroethylene in air is described in NIOSH Method S110, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat 1,2-dichloroethylene injected with a 10-µl syringe. The amount added was 0.2, 1.9, and 3.75 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 3-liter air sample at the respective level. The eluting solvent was carbon disulfide. Samples of 1,2-dichloroethylene in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,2-dichloroethylene in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 15 minutes). The "true" concentrations of 1,2-dichloroethylene in the generated samples were determined by gas chromatographic analysis using a 5 ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of 1,2-dichloroethylene. Details of the analytical procedures are given in the Analytical Procedures Section of Reference 1.

Modifications

The P&CAM 127 method was used with no major modifications.

Generation

A gas mixture of 1,2-dichloroethylene in nitrogen at twice the OSHA standard level was purchased from Matheson Gas Products. The concentration was verified by gas chromatographic analysis using bag samples for comparison. These were prepared in 4-liter Teflon® bags as described above. The test atmosphere was generated by directly sampling the mixture. The 3 concentrations were obtained by sampling only at the first stage and repeating the generation

with appropriate dilution with nitrogen for concentrations 0.5 and 1 times the OSHA standard level. Complete mixing was assured by passing the stream of analyte through 2 mixers before sampling. The total gas flow rate was 2, 4, and 8 ℓ/min for 0.5, 1, and 2 times the OSHA standard respectively. Sampling time was 15 minutes with a nominal flow rate of 200 ml/min for each charcoal tube. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation Section of Reference 2.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 1913 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred at 27 minutes. Thus the capacity of this lot of charcoal is 10.3 mg of 1,2-dichloroethylene and at the recommended sampling rate, the breakthrough volume is 5.4 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.017 \qquad \overline{CV}_2 = 0.014 \qquad \overline{CV}_T = 0.052$$

The average recovery of the generated samples over all levels was:

97.3%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: 1,2-Dichloroethylene S110

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
2.370	2.414	1.019	4.740	4.686	0.989	9.480	9.189	0.969
2.370	2.375	1.002	4.740	4.823	1.017	9.480	9.167	0.967
2.370	2.516	1.062	4.740	4.702	0.992	9.480	9.363	0.988
2.370	2.392	1.009	4.740	4.718	0.995	9.480	9.294	0.980
2.370	2.432	1.026	4.740	4.810	1.015	9.480	9.637	1.017
2.370	2.426	1.024	4.740	4.797	1.012	9.480	9.232	0.974
n =		6			6			6
mean		1.024			1.003			0.982
std dev		0.0207			0.0128			0.0184
CV_1		0.0203			0.0127			0.0187

CV_1 0.0175

$\overline{CV}_{A+\overline{DE}}$ 0.0189

Data Sheet: 1,2-Dichloroethylene S110

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.296	1.212	2.880	421.0	477	88.3
	1.291	1.208	2.880	419.4	477	87.9
	1.255	1.172	2.775	422.4	477	88.5
	1.296	1.212	2.880	420.9	477	88.2
	1.214	1.130	2.670	423.1	477	88.7
	1.228	1.144	2.820	405.8*	477	85.1*
			n = 5			
			mean	421.4		88.3
			std dev	1.44		
			CV_2	0.003		
1S	2.594	2.537	2.745	924.3	927	99.7
	2.888	2.838	3.075	923.1	927	99.6
	2.923	2.874	3.015	953.2	927	102.8
	2.618	2.562	2.730	938.6	927	101.2
	2.717	2.664	2.865	929.7	927	100.3
	2.626	2.571	2.730	941.7	927	101.6
			n = 6			
			mean	935.1		100.9
			std dev	11.62		
			CV_2	0.0124		
2S	6.184	6.228	3.255	1913.3	1913	100.0
	5.539	5.563	2.910	1911.5	1913	99.9
	5.605	5.630	2.820	1996.4	1913	104.4
	5.523	5.546	2.790	1987.8	1913	103.9
	6.014	6.052	3.045	1987.4	1913	103.9
	5.805	5.837	2.955	1975.2	1913	103.3
			n = 6			
			mean	1961.9		102.6
			std dev	38.97		
			CV_2	0.0199	$\overline{CV}_2$	0.0162

* Deleted as an outlier because this value did not pass the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

BACKUP DATA REPORT

Substance:	Chlorobromomethane, No. S113
OSHA Standard:	200 ppm (1050 mg/cu m)
Chemical used for validation:	Chlorobromomethane, Certified Gas Mixture Matheson Gas Products Bromochloromethane, reagent grade Matheson Coleman & Bell

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of chlorobromomethane in air is described in NIOSH Method S113, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with neat chlorobromomethane injected with a 10-µl syringe. The amount of solution added was 1.3, 2.5, and 5.3 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 4-liter air sample at the respective level. The eluting solvent was carbon disulfide. Samples of chlorobromomethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of chlorobromomethane in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 25 minutes). The "true" concentrations of chlorobromomethane in the generated samples were determined by gas chromatographic analysis using a 5 ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of chlorobromomethane. Details of the analytical procedures are given in the Analytical Procedures Section of Reference 1.

Modifications

The P&CAM 127 method was used with one modification. An internal standard was added for improved accuracy.

Generation

A gas mixture of chlorobromomethane in nitrogen at twice the OSHA standard level was purchased from Matheson Gas Products. The concentration was verified by gas chromatographic analysis using bag samples for comparison. These were prepared in 4-liter Teflon® bags as described above. The test atmosphere was generated by

directly sampling the mixture. The 3 concentrations were obtained by sampling only at the first stage and repeating the generation with appropriate dilution with nitrogen for concentrations 0.5 and 1 times the OSHA standard level. Complete mixing was assured by passing the stream of analyte through 2 mixers before sampling. The total gas flow rate was 2, 4, and 8 ℓ/min for 0.5, 1, and 2 times the OSHA standard respectively. Sampling time was 25 minutes with a nominal flow rate of 200 ml/min for each charcoal tube. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation Section of Reference 2.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 2315 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. Breakthrough occurred at 40 minutes. Thus the capacity of this lot of charcoal is 18.5 mg of chlorobromomethane and at the recommended sampling rate, the breakthrough volume is 8 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.051 \qquad \overline{CV}_2 = 0.028 \qquad \overline{CV}_T = 0.061$$

The average recovery of the generated samples over all levels was:

103.4%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Greenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Chlorobromomethane S113

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
3.32	3.55	1.070	6.64	6.80	1.025	13.27	12.70	0.951
3.32	3.33	1.003	6.64	6.16	0.928	13.27	11.57	0.872
3.32	3.16	0.951	6.64	6.06	0.912	13.27	11.10	0.836
3.32	3.09	0.932	6.64	5.90	0.889	13.27	11.03	0.831
3.32	3.40	1.024	6.64	6.37	0.959	13.27	12.01	0.905
3.32	3.32	1.000	6.64	6.30	0.949	13.27	11.38	0.858
n =		6			6			6
mean		0.997			0.944			0.876
std dev		0.0501			0.0470			0.0475
CV_1		0.0502			0.0498			0.0542

CV_1 0.0514

$\overline{CV}_{A+\overline{DE}}$ 0.0556

Data Sheet: Chlorobromomethane S113

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	3.224	3.196	4.800	665.9	640	104.0
	3.201	3.170	4.800	660.4	640	103.2
	3.136	3.093	4.625	668.8	640	104.5
	3.422	3.440	4.800	716.6	640	112.0
	2.946	2.864	4.450	643.6	640	100.6
	3.098	3.048	4.700	648.4	640	101.3
			n = 6			
			mean	667.3		104.3
			std dev	26.1		
			CV_2	0.0391		
1S	5.936	6.471	4.575	1414.4	1394	101.5
	6.619	7.297	5.125	1423.8	1394	102.1
	6.667	7.353	5.025	1463.2	1394	105.0
	5.986	6.533	4.550	1435.9	1394	103.0
	6.184	6.773	4.775	1418.4	1394	101.7
	5.805	6.317	4.550	1388.3	1394	99.6
			n = 6			
			mean	1424.0		102.2
			std dev	24.8		
			CV_2	0.0174		
2S	12.545	14.371	5.425	2649.0	2655	99.8
	11.592	13.228	4.850	2727.5	2655	102.7
	11.437	13.051	4.700	2776.8	2655	104.6
	11.400	13.009	4.650	2797.7	2655	105.4
	12.448	14.252	5.075	2808.2	2655	105.8
	11.930	13.638	4.925	2769.1	2655	104.3
			n = 6			
			mean	2754.7		103.8
			std dev	58.9		
			CV_2	0.0214	$\overline{CV}_2$	0.0276

* All values have passed the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

BACKUP DATA REPORT

Substance:	Bromoform S114
OSHA Standard:	0.5 ppm (5 mg/cu m)
Chemical used for validation:	Bromoform, chromatographic grade Aldrich Chemical Company, Incorporated

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with an 12.5 mg/ml solution of bromoform in n-hexane injected with a 10-µl microliter syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10-liter air sample at the respective level. The eluting solvent was carbon disulfide. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, through Pittsburgh, Pennsylvania. Gas chromatographic analysis were performed with an automatic sampler using n-pentadecane as internal standard. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1.

Modifications

The P&CAM 127 method was used with one modification. An internal standard was added for improved accuracy.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.7 liters per minute, and the rate of bromoform injection was 0.0157 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 9.7 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment 8 tubes containing charcoal only in the first portion were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration had reached only 2 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 0.5 mg of bromoform and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$\overline{CV_1} = 0.0432$ $\overline{CV_2} = 0.0469$ $\overline{CV_T} = 0.071$

The average recovery of the generated samples over all levels was:

98.5

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.
3. Documentation of NIOSH Validation Tests, ibid.

Data Sheet: Bromoform S114

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
0.025	0.021	0.843	0.050	0.042	0.832	0.100	0.093	0.930
0.025	0.021	0.837	0.050	0.046	0.929	0.100	0.091	0.914
0.025	0.020	0.789	0.050	0.040	0.800	0.100	0.090	0.895
0.025	0.019	0.777	0.050	0.044	0.881	0.100	0.089	0.894
0.025	0.019	0.778	0.050	0.047	0.938	0.100	0.090	0.901
0.025	0.019	0.771	0.050	0.045	0.892	0.100	0.090	0.898
n =		6			6			6
mean		0.799			0.879			0.905
std dev		0.032			0.054			0.014
CV_1		0.040			0.061			0.015

CV_1 0.043

$\overline{CV}_{A+\overline{DE}}$ 0.047

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Data Sheet: Bromoform S114

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.022	0.027	9.600	2.79	2.80	99.7
	0.024	0.029	9.600	3.00	2.80	107.1
	0.023	0.028	9.250	3.01	2.80	107.5
	0.023	0.028	9.600	2.90	2.80	103.6
	0.022	0.027	8.900	3.02	2.80	107.9
	0.024	0.029	9.400	3.06	2.80	109.4
			n = 6			
			mean	2.96		105.9
			std dev	0.101		
			CV_2	0.0339		
1S	0.046	0.052	9.150	5.65	5.50	102.7
	0.048	0.054	10.250	5.29	5.50	96.2
	0.048	0.054	10.050	5.35	5.50	97.3
	0.038	0.044	9.100	4.85	5.50	88.2
	0.051	0.057	9.550	5.97	5.50	108.6
	0.044	0.050	9.100	5.50	5.50	100.0
			n = 6			
			mean	5.44		98.8
			std dev	0.377		
			CV_2	0.0693		
2S	0.094	0.104	10.850	9.58	11.00	87.1
	0.090	0.100	9.700	10.26	11.00	93.3
	0.086	0.095	9.400	10.11	11.00	91.9
	0.086	0.095	9.300	10.21	11.00	92.8
	0.091	0.100	10.150	9.86	11.00	89.6
	0.089	0.098	9.850	9.95	11.00	90.4
			n = 6			
			mean	9.97		90.9
			std dev	0.254		
			CV_2	0.0255	CV_2	0.0469

BACKUP DATA REPORT

Substance: Benzyl chloride, No. S115

OSHA Standard: 1 ppm (5 mg/cu m)

Chemical used for validation: Benzyl chloride, 97%
Aldrich Chemical Company, Inc.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of benzyl chloride in air is described in NIOSH Method S115, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 12.5 mg/ml solution of benzyl chloride in heptane injected with a 10-µl syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 10-liter air sample at the respective level. The eluting solvent was carbon disulfide.

To study the change of desorption efficiency with varying time of standing before desorption a number of desorption samples at the OSHA standard level were prepared as described above. Groups of 4 samples were analyzed after 1, 2, and 7 days. The results, tabulated below showed no significant decrease in the period studies.

Time Before Desorption, Days	Desorption Efficiency, %
1	86.5
2	85.5
7	84.1

Samples of benzyl chloride in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of benzyl chloride in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 50 minutes). The "true" concentrations of benzyl chloride in the generated samples were determined by gas chromatographic analysis using a 5-ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of benzyl chloride. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels did not increase with increasing concentration and differed by less than one standard deviation. Therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with one modification. An internal standard was added for improved accuracy.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous 3-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.6 liters per minute, and the rate of benzyl chloride injection was 0.0114 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at 2 times the OSHA standard level (actual concentration was 8.1 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5 percent of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, 8 tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the 8 tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration had reached only 2 percent of the test atmosphere concentration. Thus the capacity of this lot of charcoal exceeds 0.39 mg of benzyl chloride and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.031 \qquad \overline{CV}_2 = 0.081 \qquad \overline{CV}_T = 0.096$$

The average recovery of the generated samples over all levels was:

93.1%

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Sarkan, A. E., and Breenburg, B. G., Contributions to Order Statistics, New York, John Wiley & Sons, 1962, p. 302.

Data Sheet: Benzyl Chloride S115

Analysis

Level	0.5S			1S			2S	
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
.0250	.0224	0.898	.0500	.0458	0.917	.1000	.0929	0.929
.0250	.0224	0.895	.0500	.0461	0.921	.1000	.0942	0.942
.0250	.0230	0.921	.0500	.0461	0.923	.1000	.0931	0.931
.0250	.0235	0.939	.0500	.0452	0.904	.1000	.0874	0.874
.0250	.0222	0.886	.0500	.0438	0.876	.1000	.0881	0.881
.0250	.0212	0.848	.0500	.0445	0.890	.1000	.0874	0.874
n =		6			6			6
mean		0.898			0.905			0.905
std dev		0.0312			0.0187			0.0320
CV_1		0.0348			0.0207			0.0354

$$\frac{CV_1}{\overline{CV}_{A+DE}} \quad 0.310 \quad 0.0335$$

Data Sheet: Benzyl Chloride S115

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.0166	0.0183	9.60	1.911	1.8	106.2
	0.0166	0.0183	9.60	1.911	1.8	106.2
	0.0147	0.0162	9.25	1.756	1.8	97.6
	0.0155	0.0172	9.60	1.791	1.8	99.5
	0.0137	0.0151	8.90	1.701	1.8	94.5
	0.0130	0.0143	9.40	1.526	1.8	84.8
			n = 6			
			mean	1.766		98.1
			std dev	0.145		
			CV_2	0.0819		
1S	0.0319	0.0353	9.15	3.859	3.9	98.9
	0.0361	0.0400	10.25	3.905	3.9	100.1
	0.0346	0.0383	10.05	3.812	3.9	97.8
	0.0272	0.0301	9.10	3.307	3.9	84.8
	0.0291	0.0323	9.55	3.380	3.9	86.7
	0.0211	0.0234	9.10	2.567*	3.9	65.8*
			n = 5			
			mean	3.65		93.66
			std dev	0.285		
			CV_2	0.0780		
2S	0.0760	0.0842	10.85	7.756	8.1	95.8
	0.0673	0.0746	9.70	7.686	8.1	94.9
	0.0620	0.0687	9.40	7.310	8.1	90.2
	0.0560	0.0620	9.30	6.669	8.1	82.3
	0.0578	0.0640	10.15	6.303	8.1	77.8
	0.0610	0.0675	9.85	6.857	8.1	84.7
			n = 6			
			mean	7.10		87.6
			std dev	0.583		
			CV_2	0.0821	$\overline{CV}_2$	0.081

* Deleted as an outlier, because this value did not pass the Grubb's outlier test at the 1% confidence level as described in Reference No. 4.

Backup Data Report

Substance:	Allyl Chloride, No. S116
OSHA Standard:	1 ppm (3 mg/cu m)
Chemical used for validation:	Allyl Chloride, Lot 22 MC/B

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of allyl chloride in air is described in NIOSH Method S116, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100-mg portions of charcoal with the appropriate amounts of liquid allyl chloride to represent 100-liter air samples. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector (Reference No. 1). Samples of allyl chloride in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with benzene and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.), and the "found" concentrations of allyl chloride in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample x 100 minutes). The concentration of the analyte in the generator was determined by a gas chromatograph and by comparison with a "bag" standard. Using the flow rate of the dilution air into the 2X chamber and the concentration of analyte in the effluent from the generator, the "true" concentration of allyl chloride at 2X the OSHA standard was determined. Known dilution factors were used to calculate the "true" concentrations at the 1.0X and 0.5X OSHA standard levels.

Modification

There were two major modifications to P&CAM 127.

Benzene was used as the desorbing solvent for the method instead of carbon disulfide. (See Discussion Section.)

A hexane solution containing 7.5 mg/ml of allyl chloride was used to apply the analyte to the charcoal. This was done so it would not be necessary to inject less than 2 microliters at the 0.5X level.

Generation

Samples of allyl chloride in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 1). The lower section of the generator was placed in a dry ice-

acetone bath kept at -78.5°C. Nitrogen gas was passed through a drying tube into the bottom of the generator at a flow rate of 0.778 liter per minute. The vapor-saturated nitrogen was diluted using dilution air at a flow rate of 17.6 liters per minute to obtain a concentration of 76.5 mg/cu m. This concentration was measured with a gas chromatograph which was standardized with bag standards. The allyl chloride vapor was further diluted by addition of air at a rate of 176.7 liters per minute to obtain a concentration of 7.19 mg/cu m in the 2X sampling chamber. Known dilution factors were applied to obtain the "taken" concentration at the 1.0X and 0.5X OSHA standard levels.

Samples of allyl chloride were collected for 100 minutes at a rate of approximately 1 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted at a concentration of 7.56 mg/cu m at an average flow of 0.913 liter per minute. It was not possible to measure allyl chloride from the breakthrough tubes with a gas chromatograph or a total hydrocarbon analyzer, because the concentration of allyl chloride being sampled was too low. Therefore, the breakthrough test was done in the following manner. A set of 12 tubes containing both front and backup sections were used. After 90 minutes of sampling, and every 30 minutes thereafter up to 240 minutes, two tubes were removed from the sampling chamber. The backup sections were then desorbed with benzene and analyzed. The results are given in the following table:

Sample time	Calculated mg added to the charcoal tube	mg found on backup section
90 minutes	0.62	Sample lost in analysis
90 minutes	0.65	-0-
120 minutes	0.89	-0-
120 minutes	0.82	-0-
150 minutes	1.04	-0-
150 minutes	1.00	-0-
180 minutes	1.24	0.016
180 minutes	1.24	0.021
210 minutes	1.50	0.021
210 minutes	1.45	0.057
240 minutes	1.71	Sample lost in analysis
240 minutes	1.74	0.19

From the above data, it appears that the sample size should be controlled to collect a maximum of 1.5 mg in order to be confident that less than 5% is on the backup section of the charcoal tubes.

Discussion

It was necessary to choose an eluent for desorbing allyl chloride from the charcoal, because carbon disulfide gave a peak that interferred with the allyl chloride peak on the gas chromatogram. The GC conditions used were as follows:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 185°C injector temperature
5. 250°C detector temperature
6. 160°C column temperature

A 4-ft X 1/4-in stainless steel column packed with 50/80 mesh Porapak Q was used.

Methanol was tested, and the average recovery at 1X the OSHA standard was 0.741.

Benzene (reagent grade) was also tested, and the average recovery at 1X the OSHA standard was 0.934. Benzene was therefore used as the eluent for the method.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for allyl chloride as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 9.6 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for allyl chloride show excellent precision. Therefore, pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the data for the three levels.

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.023$ $\overline{CV}_2 = 0.049$ $\overline{CV}_T = 0.071$

The average recovery at the OSHA standard level was 99.7%.

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Allyl Chloride, S116

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.150	0.1392	0.928	0.300	0.2829	0.943	0.600	0.589	0.982
0.150	0.1388	0.925	0.300	0.2770	0.923	0.600	0.592	0.987
0.150	0.1373	0.915	0.300	0.2774	0.925	0.600	0.566	0.943
0.150	0.1452	0.968	0.300	0.2939	0.980	0.600	0.570	0.950
0.150	0.1412	0.941	0.300	0.2812	0.937	0.600	0.575	0.958
0.150	0.1388	0.925	0.300	0.2697	0.899	0.600	0.572	0.953
n =		6			6			6
mean		0.934			0.934			0.962
std dev		0.019			0.027			0.018
CV_1		0.020			0.029			0.019

$\overline{CV}_1$ 0.023

$\overline{CV}_{A+\overline{DE}}$ 0.025

The equation D.E. = $0.949 - e^{-29.1 \times mg}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 4.

Data Sheet: Allyl Chloride, S116

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.1732	0.1837	94.4	1.946	1.801	
	0.1714	0.1820	88.9	2.047	1.801	
	0.1784	0.1892	94.5	2.002	1.801	
	0.1709	0.1814	91.9	1.974	1.801	
	0.1838	0.1947	96.5	2.018	1.801	
	0.1911	0.2022	99.9	2.024	1.801	
			n = 6			
			mean	2.002		111.2
			std dev	0.037		
			CV_2	0.018		
1S	0.295	0.311	92.1	3.38	3.60	
	0.320	0.337	91.6	3.68	3.60	
	0.338	0.356	96.9	3.67	3.60	
	0.328	0.346	96.3	3.59	3.60	
	0.303	0.319	89.4	3.57	3.60	
	0.318	0.335	91.6	3.66	3.60	
			n = 6			
			mean	3.59		99.7
			std dev	0.11		
			CV_2	0.031		
2S	0.666	0.702	93.0	7.55	7.19	
	0.702	0.740	93.6	7.91	7.19	
	0.571	0.602	91.9	6.55	7.19	
	0.740	0.780	95.0	8.21	7.19	
	0.692	0.729	94.2	7.74	7.19	
	(Sample was lost.)					
			n = 5			
			mean	7.59		105.6
			std dev	0.63		
$\overline{CV}_2$	0.049		CV_2	0.083		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W.J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Acetylene Tetrabromide, No. S117
OSHA Standard:	1 ppm (14 mg/cu m)
Chemical used for validation:	Acetylene Tetrabromide, Lot 042347 Aldrich Chemical Company

Procedure

The procedure for collecting and analyzing concentrations of acetylene tetrabromide in air is described in NIOSH Method S117, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150 mg portions of silica gel* with the appropriate amounts of acetylene tetrabromide to represent 100-liter air samples. Samples of acetylene tetrabromide in air were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with tetrahydrofuran and analyzed by gas chromatography. The amounts measured were corrected for D.E. to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 107 minutes). The "true" concentration at 2X, 1X, and 0.5X OSHA standard levels were determined from the delivery rate of the syringe drive and the flow rates of the dilution air.

Modifications

Three major modifications were made to P&CAM 127. The samples were collected on silica gel tubes. A hexane solution of acetylene tetrabromide (350 mg/ml) was used to apply the analyte to the silica gel, so it would not be necessary to inject less than 2 µl at the 0.5X level. The analyte was desorbed with tetrahydrofuran. The reasons for these modifications are discussed in the Discussion Section of this report.

Generation

Samples of acetylene tetrabromide were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe-drive pump. A 15-inch long stainless steel needle was attached to the syringe. The other end of the needle passed through a rubber septum into a heated glass tube maintained at 200°C.

* Silica gel tubes were obtained from Environmental Compliance Corp., Venetia, Pa., Catalog 226-10.

The tube was packed with glass beads to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 13.59 liters/minute and diluted with air at a rate of 22.33 liters/minute immediately after the heated zone. This concentration was monitored by a total hydrocarbon analyzer. Further dilution with air at a rate of 177.19 liters/minute was made to obtain the 2X OSHA level. Dilutions were again made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1.

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using the rate of delivery of the syringe drive and the flow rates of the dilution air.

Samples were collected for 107 minutes at a rate of approximately 1.0 liter per minute (individual critical orifices vary slightly in flow rate.)

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2. A total hydrocarbon analyzer was used. Less than 5% of the generated concentration of 28.14 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 1 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

Preliminary desorption efficiency tests were conducted at 1X the OSHA standard level, using charcoal Lot 105 and carbon disulfide as the desorbing solvent. The results are given below:

DESORPTION EFFICIENCY TESTS OF ACETYLENE TETRABROMIDE
ON CHARCOAL LOT 105
(FOR A 10-LITER SAMPLE)

Solvent	mg taken	mg found	Desorption Efficiency
CS_2 (1 ml)	0.1421	0.0375	0.264
CS_2 (1 ml)	0.1421	0.0350	0.246

The GC conditions that were used for the experiment were as follows:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 220°C injector temperature
5. 270°C manifold temperature (detector)
6. 105°C column temperature

A glass column (3-ft x 1/4-in) packed with 5% SE-30 on 80/100 mesh Gas Chrom W was used.

Using the above GC conditions, additional desorption efficiency tests were conducted at 1X the OSHA standard level, using charcoal Lot 104. The results are given in the following table:

DESORPTION EFFICIENCY OF ACETYLENE TETRABROMIDE
ON CHARCOAL LOT 104

(FOR A 10-LITER SAMPLE)

Solvent (1 ml)	mg taken	mg found	Desorption Efficiency
Benzene	0.1421	0.0547	0.385
Methylene Chloride	0.1421	0.0273	0.192
Methanol	0.1421	-0-	-0-
Acetone	0.1421	0.0383	0.270
Tetrahydrofuran	0.1421	0.0616	0.433
Ethyl Acetate	0.1421	0.0437	0.308

Because of the poor recoveries of acetylene tetrabromide on charcoal, silica gel was used to collect the analyte.

Preliminary desorption efficiency trials were conducted on silica gel. The concentrations were measured using the same GC conditions as stated above. It was decided at this time to increase the sample size from 10 liters to 100 liters to increase the GC sensitivity. Carbon disulfide, benzene, and tetrahydrofuran were tested as possible desorbing solvents. Based on these results, tetrahydrofuran was chosen. Results, using a 100-liter sample and tetrahydrofuran as the desorbing solvent, are given in the Data Sheets at the end of this report.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.041$ $\overline{CV}_2 = 0.080$ $\overline{CV}_T = 0.096$

The average recovery at the OSHA standard level was 96.5%.

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Acetylene Tetrabromide S117

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.700	0.522	0.746	1.399	1.233	0.881	2.798	2.794	0.999
0.700	0.560	0.800	1.399	1.286	0.919	2.798	2.816	1.006
0.700	0.578	0.826	1.399	1.269	0.907	2.798	2.792	0.998
0.700	0.504	0.720	1.399	1.295	0.926	2.798	2.800	1.001
0.700	0.549	0.784	1.399	1.316	0.941	2.798	2.680	0.958
0.700	0.588	0.840	1.399	1.333	0.953	2.798	2.630	0.940
n =		6			6			6
mean		0.786			0.921			0.984
std dev		0.046			0.025			0.028
CV_1		0.059			0.027			0.028

$\overline{CV}_1$ 0.041

$\overline{CV}_{A+\overline{DE}}$ 0.044

The equation D.E. = $0.966 - e^{-3.05 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 4.

Data Sheet: Acetylene Tetrabromide S117

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.436	0.622	99.5	6.25	7.04	
	0.431	0.618	97.3	6.35	7.04	
	0.476	0.650	98.8	6.58	7.04	
	0.338	0.550	95.6	5.75	7.04	
	0.486	0.658	97.3	6.76	7.04	
	0.604	0.748	99.5	7.52	7.04	
			n = 6			
			mean	6.54		92.9
			std dev	0.59		
			CV_2	0.090		
1S	1.435	1.506	95.9	15.70	14.07	
	1.233	1.308	100.4	13.03	14.07	
	1.322	1.395	101.1	13.80	14.07	
	1.189	1.266	94.4	13.41	14.07	
	1.187	1.264	101.1	12.50	14.07	
	1.137	1.216	93.1	13.06	14.07	
			n = 6			
			mean	13.58		96.5
			std dev	1.12		
			CV_2	0.082		
2S	2.409	2.496	98.8	25.26	28.14	
	2.302	2.385	97.7	24.41	28.14	
	2.266	2.348	96.9	24.23	28.14	
	1.981	2.055	96.9	21.21	28.14	
	2.127	2.206	98.8	22.33	28.14	
	2.235	2.316	102.7	22.55	28.14	
			n = 6			
			mean	23.33		82.9
			std dev	1.54		
$\overline{CV}_2$ 0.080			CV_2	0.066		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Epichlorohydrin, No. S118
OSHA Standard:	5 ppm (20 mg/cu m)
Chemical used for validation:	Epichlorohydrin, Lot #325814 J.T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of epichlorohydrin in air is described in NIOSH Method S118, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid epichlorohydrin to represent 20-liter air samples. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. The use of the automatic sample injector is described in the attachment to this report. Samples of epichlorohydrin in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of epichlorohydrin in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 109.3 minutes). The "true" concentrations of epichlorohydrin in the generated samples were determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There was only one major modification to P&CAM 127 which was in the preparation of the samples for desorption efficiency tests. A hexane solution of epichlorohydrin containing 94.5 mg/ml was used to apply the analyte to the charcoal. This was done so it would not be necessary to inject less than 2 microliters at the 0.5X level.

Generation

Samples of epichlorohydrin in air were generated by the procedure described in the attachment to this report. The generator conditions used are given in the following table:

Generator Conditions
for
Epichlorohydrin

Nitrogen flow rate	0.172 liters/minute at 23°C
Dilution air flow rate	65.9 liters/minute at 23°C
Bath temperature	0°C

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 1). Samples were collected for 109.3 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 1). Less than 5% of the generated concentration of 43.1 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.185 liter per minute, indicating a capacity of at least 2 mg of epichlorohydrin in the charcoal tube.

Discussion

A time study on the storage stability of epichlorohydrin on charcoal Lot 105 was made. Tests were done at 1X the OSHA standard level by spiking 0.378 mg of epichlorohydrin onto 100 mg of charcoal Lot 105. Two samples each of epichlorohydrin on charcoal were allowed to stand for a time period of 23, 95, and 143 hours before sample analysis. The results are summarized in Table 1.

Table 1

Time on Charcoal before Analysis (hours)	mg taken	mg found	D.E.
143	0.378	0.321	0.849
143	0.378	0.331	0.876
95	0.378	0.328	0.868
95	0.378	0.333	0.881
23	0.378	0.341	0.902
23	0.378	0.345	0.913

From the above results it appears that epichlorohydrin is stable on charcoal for 143 hours.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.031$ $\overline{CV}_2 = 0.025$ $\overline{CV}_T = 0.057$

The average recovery at the OSHA standard level was 99.3%. However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Epichlorohydrin, S118

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.1890	0.1651	0.874	0.378	0.352	0.931	0.756	0.675	0.893
0.1890	0.1698	0.898	0.378	0.341	0.902	0.756	0.695	0.919
0.1890	0.1732	0.916	0.378	0.334	0.884	0.756	0.667	0.882
0.1890	0.1601	0.847	0.378	0.343	0.907	0.756	0.716	0.947
0.1890	0.1737	0.919	0.378	0.346	0.915	0.756	0.712	0.942
0.1890	0.1735	0.918	0.378	0.323	0.854	0.756	0.712	0.942

n =	6	6	6
mean	0.895	0.899	0.921
std dev	0.029	0.027	0.028
CV_1	0.032	0.030	0.030

$\overline{CV}_1$ 0.031

$\overline{CV}_{A+\overline{DE}}$ 0.033

The equation D.E. = $0.911 - e^{-23.5 \times \text{mg found}}$ was used to calculate the corr mg in the sampling and analysis table. A program for the use of this equation is documented in Reference No. 3.

Data Sheet: Epichlorohydrin, S118

Sampling and Analysis

Test Level	Found mg	Found Corr mg	Found Liters	Found mg/cu m*	Taken mg/cu m	Recovery
0.5S	0.2231	0.2462	20.55	11.98	11.70	
	0.2386	0.2628	21.97	11.96	11.70	
	0.2281	0.2512	20.99	11.97	11.70	
	0.2511	0.2762	22.73	12.15	11.70	
	0.2225	0.2456	20.88	11.76	11.70	
	0.2378	0.2619	21.64	12.10	11.70	
			n = 6			
			mean	11.99		102.5
			std dev	0.14		
			CV_2	0.012		
1S	0.372	0.408	19.13	21.33	22.99	
	0.403	0.442	19.13	23.10	22.99	
	0.387	0.425	18.25	23.29	22.99	
	0.371	0.407	17.93	22.70	22.99	
	0.418	0.459	19.46	23.59	22.99	
	0.359	0.394	17.16	22.96	22.99	
			n = 6			
			mean	22.83		99.3
			std dev	0.79		
			CV_2	0.035		
2S	0.872	0.957	19.89	48.1	43.1	
	0.915	1.004	20.55	48.9	43.1	
	0.905	0.993	20.22	49.1	43.1	
	0.865	0.950	20.22	47.0	43.1	
	0.854	0.937	20.33	46.1	43.1	
	0.876	0.962	20.22	47.6	43.1	
			n = 6			
			mean	47.8		110.9
			std dev	1.1		
$\overline{CV}_2$ 0.025			CV_2	0.023		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W.J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Attachment to Epichlorohydrin S118 Backup Data Report

Gas Chromatograph with an Automatic Sample Injector

The equipment consists of a Microtek MT 220 gas chromatograph, a Varian Model 8000 automatic sample injector and a HP 3380A computing integrator. The Model 8000 automatic sample injector is mounted vertically on the Microtek MT 220. The autosampler has a rotating carousel module which can hold 60 sample vials (2-ml glass vials with screw tops and Teflon-lined septa), an injector module with an adjustable side-arm syringe pneumatically actuated by compressed air, and a control unit which permits total automation in a closed loop form with a computer. For this program, the syringe injector is set to deliver 5 microliters of sample solution. The unit was tested to verify that sample to sample cross-contamination does not occur and that the reproducibility of the sample injection is adequate.

Spiked samples are prepared by adding a known amount of the analyte to 100 mg of charcoal, SKC, Lot 105. The analyte added is equivalent to that which would be found in a fixed volume of air, containing the analyte in concentrations of 0.5X, 1X, and 2X the OSHA standard. A set of eighteen spiked samples are prepared, i.e. six samples for each concentration level.

The spiking experiments are done in the automatic sample injector vials loaded with 100 mg of charcoal obtained from bottled batches of the same Lot 105 charcoal. The spiked charcoal vials are stored for at least an overnight period but normally not more than 2 days. The analyte is desorbed from the charcoal by adding 1.0 ml of carbon disulfide to the sample injector vials. The sample vials are allowed to stand for at least 30 minutes with periodic shaking, and the vials are then loaded into the automatic sample injector tray. Five microliter aliquots of these samples are analyzed using GC conditions appropriate for the analyte. Two injections from each vial are taken, and an average "mg found" is computed.

The desorption efficiency determined for the 18 spiked samples are plotted against "mg found" to obtain a D.E. curve. The respective D.E. is used to calculate the corrected mg for the generated samples of analyte in the sample. The concentration of analyte in air "found" is determined by dividing the corrected mg found by the sample volume.

Vapor Generation System

The system for generating and collecting samples of vapor from volatile liquids consists of a sample generator, a mixing and dilution section, and three sampling chambers. Samples are generated at a concentration of 2X the OSHA standard, serial dilutions are made to 1X and 0.5X the standard, and samples are collected simultaneously at the three concentrations.

The vapor generator was adapted from the apparatus described in Reference No. 1 which describes a method that has been used to measure the vapor pressure of liquids. A schematic diagram of this vapor generator is shown in Figures 1 and 2. The vapor generator consists of two sections--a generating section (Figure 1) and a diluting section (Figure 2) which are connected by a ground glass joint.

The generating section (Figure 1) consists of a pyrex glass tube which is 2.4 cm in diameter and 19.5 cm long. A coarse glass frit is sealed in the bottom of the tube. The bottom of this tube is connected to a 7-mm O.D. glass tube which is bent 180° and extends up until it is nearly as high as the larger tube. The sample, which may be either a liquid or low melting solid, is introduced into the large tube. This part of the apparatus is immersed in a thermostated bath with the analyte level below the bath level. Nitrogen gas is introduced through the small tube and passes through the frit. The small bubbles, which form at the frit, rise through the liquid and become saturated or nearly saturated with the vapor of the liquid. The bath temperature and the flow of nitrogen determine the actual amount of vapor generated. Increasing either the nitrogen flow or the bath temperature, increases the amount of vapor generated.

The diluting section (Figure 2) of the vapor generator consists of a pyrex glass tube which is 2.4 cm in diameter and 13 cm high. The dilution air is introduced through a 7-mm O.D. glass tube connected to the side of the diluting tube. Sufficient air is added to dilute the vapor in nitrogen to the desired concentration. Vapor saturation of the air stream must not be exceeded to produce a well-mixed stream.*

The equations given in Reference No. 1 can be used to determine the approximate vapor concentration in the saturated nitrogen stream. The actual concentration of the vapor in each chamber in the generator should be measured using either a Beckman Model 402 total hydrocarbon analyzer or a gas chromatograph. Bag standards are used to calibrate the instrument used.

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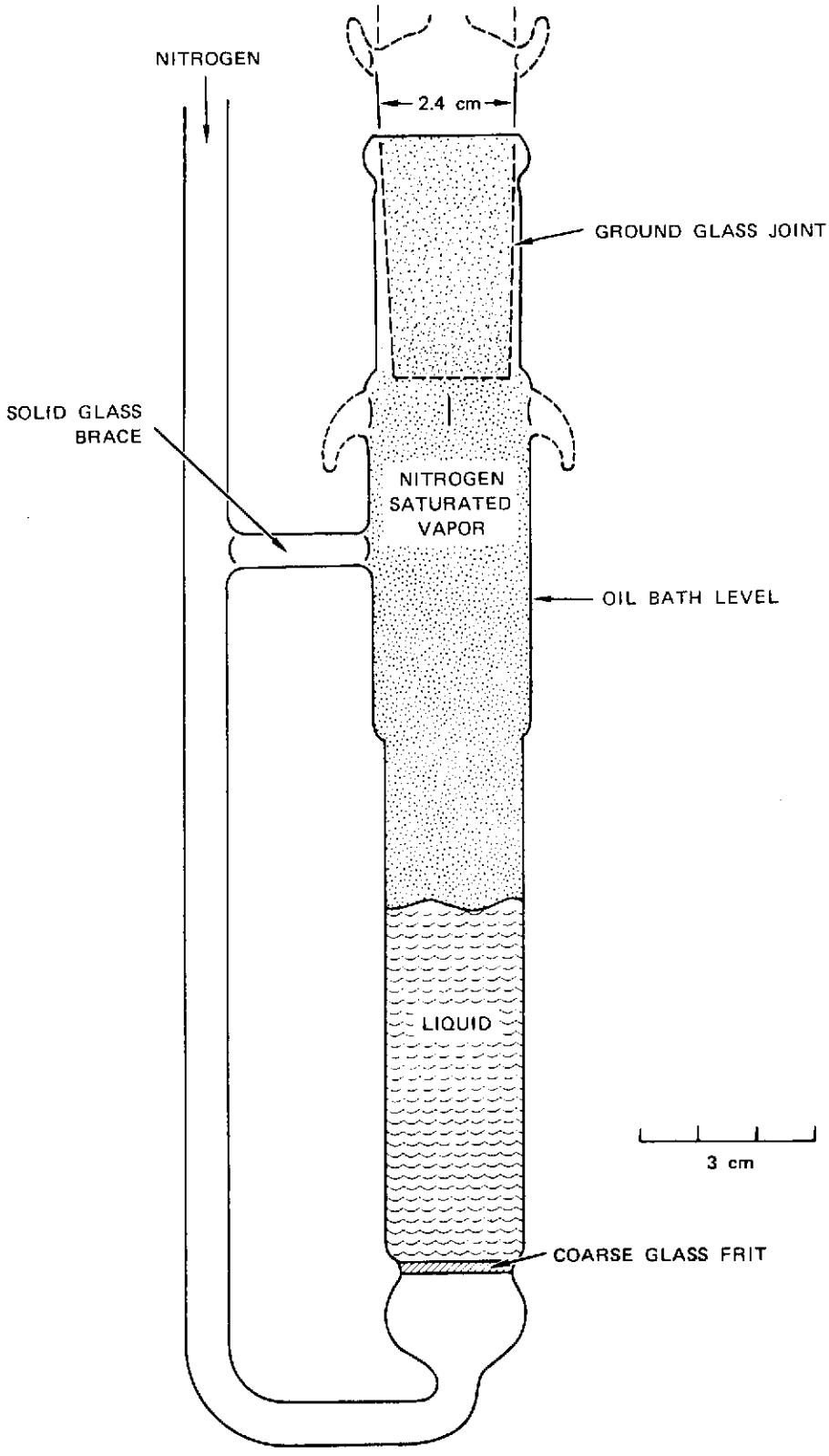
*If the vapor saturation concentration is exceeded, particles will be formed in the cool air stream.



NOTE: Apparatus is immersed in a thermostated bath.

FIGURE 1 VAPOR GENERATOR (generating section)

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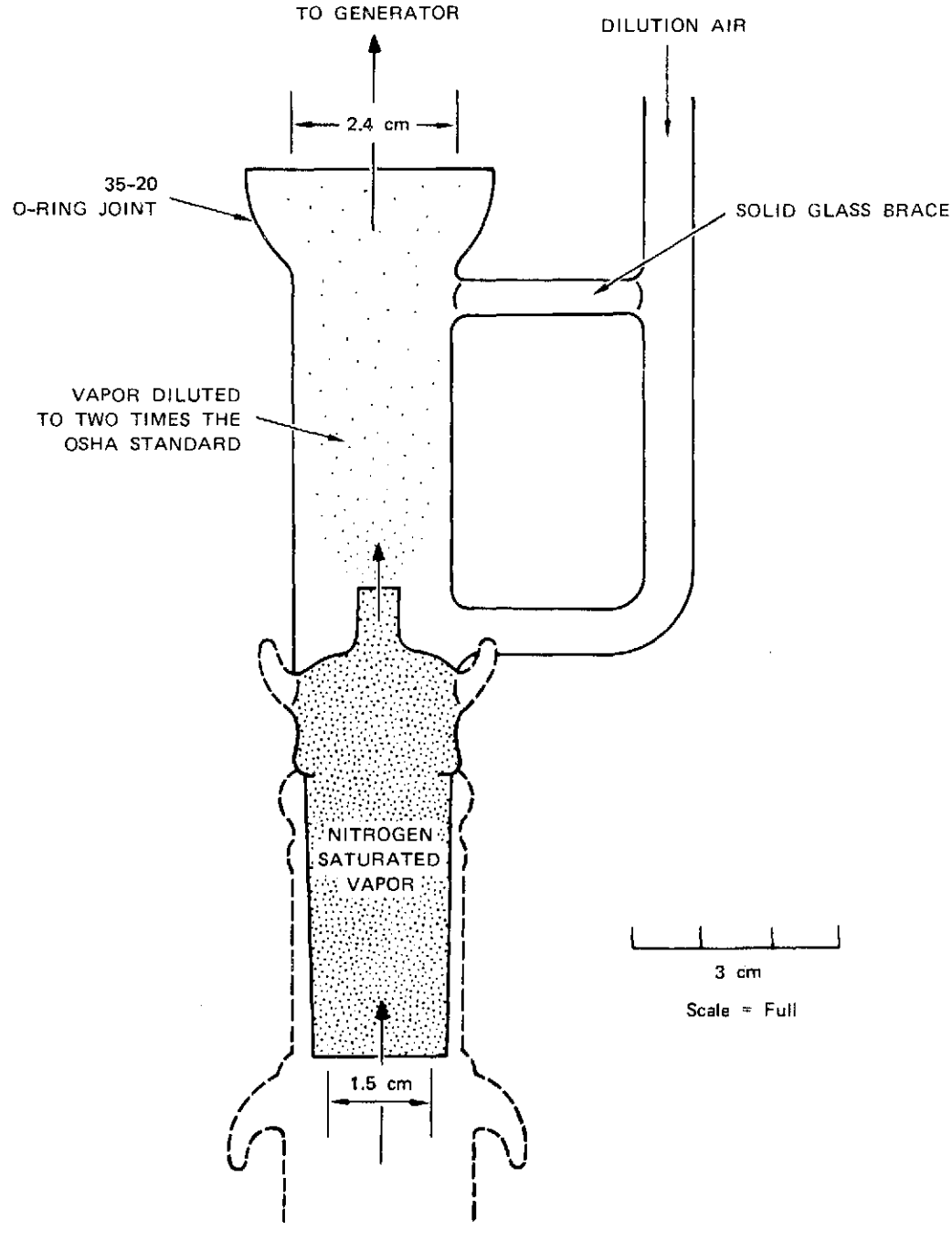

FIGURE 2 VAPOR GENERATOR (diluting section)

In the sample generator two sets of matched orifices are used to control the gas flow rates in drawing the vapors into the sampling chambers and to regulate the gas flow rates used to make secondary dilutions.

After primary dilution, the vapor at 2X the standard concentration enters a stainless steel transfer line, the other end of which is connected to a pump through a critical orifice. The three sampling chambers branch off this line. The generated vapor is split at the first sampling chamber by a pump connected through a critical orifice to the bottom of the first chamber. This chamber now contains an atmosphere at approximately 2X the standard as generated. Diluting air enters the transfer line immediately following the branch-off to the first chamber, mixes with the vapor sample, and the vapor at the new concentration of approximately 1X the standard is again split by pumping into the second chamber. Another dilution is made in the transfer line following the second chamber to obtain the approximate concentration needed for the 0.5X level. A pump connected to the bottom of the third sampling chamber pulls sample at this concentration into this chamber.

The two sets of orifices used to obtain these dilutions have been chosen so that the desired flow patterns are maintained in the system, and so the appropriate dilutions are made between the first and second, and second and third chambers. The orifices connected to the outlet of the transfer line and to the three sampling chambers operate at 13.5 liters per minute. The pressure of the secondary dilution air entering the line between the chambers is set so that each orifice admits air at a flow of 13.5 liters per minute. On the basis of the orifice calibrations, the concentration in the 1X chamber is 0.500 times the concentration in the 2X chamber, and the concentration in the 0.5X chamber is 0.250 times the concentration in the 2X chamber.

The three sampling chambers are physically identical. Each consists of a stainless steel cone, the top of which is connected to the transfer line, and the bottom of which is fitted to a cylindrical section. The base of the cylindrical section contains the fittings necessary to hold six samples in a vertical position, plus a centered outlet to the pump mentioned above. The six sample ports are connected through six matching critical orifices to a sampling pump. A separate metal bellows vacuum pump is used for sampling each chamber.

Generation of vapors at the desired concentration is accomplished by adjusting the flows of nitrogen gas through the generating flask and of the primary dilution air. Adjustments for further dilutions to the 1X and 0.5X levels are not necessary since this secondary dilution is controlled automatically by the system of orifices described above.

References

1. Physical Methods of Chemistry, Part V, A. Weissberger and B.W. Rossiter, eds. 61-66, (John Wiley & Sons, 1971).

Backup Data Report

Substance:	Chlorinated Diphenyl Oxide, No. S119
OSHA Standard:	0.5 mg/cu m
Chemical Used for Validation:	Chlorinated Diphenyl Oxide Chem Samples

Procedure

The general procedure used is described in NIOSH Method No. S119. The reliability of the analytical method was tested at sample concentrations equal to that present in a 90-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot (2, 4, and 8 microliters) of a 112.75 mg/10 ml solution of chlorinated diphenyl oxide in benzene was added to 37-mm type AA Millipore filters. Chlorinated diphenyl oxide was extracted from the filter with iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector. The results of the analysis of these samples are given in the Analysis table. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S119. Test atmospheres of chlorinated diphenyl oxide at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on the Millipore filters. The results of analysis of these samples are given in the Sampling and Analysis table. The estimated average size of the particles was 1 micron diameter.

Generation

Samples of chlorinated diphenyl oxide in air were generated by the procedure described in Reference No. 1.

A 0.5% solution of chlorinated diphenyl oxide in toluene (5.0 g of chlorinated diphenyl oxide made up to a 1-liter volume with toluene) was used in the aspiration system for the generation of the 2X samples. A 0.25% solution of the analyte in toluene was used in the aspiration system for generation of the 1X and 0.5X samples. Samples of chlorinated diphenyl oxide were generated and collected separately at each of the three levels.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples collected for at least ten minutes, and these samples analyzed. The results of the analyses were used to select new conditions to reach the required concentration. When the desired concentration was reached, six samples at each level were collected. Samples were collected for one hour at a rate of approximately 1.5 liters/minute.

Collection Efficiency

Collection efficiency at a concentration of 0.965 mg/cu m was determined by measuring the amount of particulate collected on each of the two filters in series mounted in direct contact with each other. This test was done on each of the six samples taken for validation at the 2X level. The collection efficiency of the filter was found to be 1.00 at a detection limit of 0.0020 mg/cu m. Thus, no correction for collection efficiency is needed in this method. The results of the collection efficiency test are presented below:

Concentration in First Filter	Concentration in Second Filter	Collection Efficiency
0.996 mg/cu m	N.D.*	1.00
1.015 mg/cu m	"	1.00
0.979 mg/cu m	"	1.00
0.927 mg/cu m	"	1.00
0.929 mg/cu m	"	1.00
0.943 mg/cu m	"	1.00

*N.D. = Not detected at a detection limit of 0.0020 mg/cu m.

Discussion

The following experiment was conducted to ascertain whether filter collection would be appropriate. Four filters were spotted with 99.6 micrograms of chlorinated diphenyl oxide, using the same stock solutions used for analytical method recovery tests. After air drying to allow the solvent to evaporate, 100 liters of air was pulled through the filters at a flow rate of 1.5 liter/minute. The filters were then analyzed, with the following results:

	µg added	µg found	Recovery
1	99.6	98.5	0.99
2	99.6	101.1	1.02
3	99.6	99.2	1.00
4	99.6	98.2	0.98

From these results, it was concluded that the analyte would be present as a particulate, it would not be vaporized from the filter after collection, and filter collection was selected.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.019$ $\overline{CV}_2 = 0.048$ $\overline{CV}_T = 0.070$

Data Sheet: Chlorinated Diphenyl Oxide S119

Analysis

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
22.56	22.24	0.986	45.1	45.4	1.007	90.2	89.6	0.993
22.56	23.54	1.043	45.1	46.1	1.022	90.2	89.6	0.993
22.56	22.13	0.981	45.1	46.7	1.036	90.2	90.0	0.998
22.56	23.15	1.026	45.1	45.0	0.998	90.2	91.0	1.009
22.56	23.17	1.027	45.1	45.9	1.018	90.2	90.9	1.008
22.56	23.81	1.055	45.1	45.9	1.018	90.2	90.6	1.004
n =		6			6			6
mean		1.020			1.016			1.001
std dev		0.030			0.013			0.007
CV_1		0.029			0.013			0.007

$\overline{CV}_1$ 0.019

$\overline{CV}_{A+\overline{AMR}}$ 0.021

Based on the above results, no Analytical Method Recovery correction is necessary.

Data Sheet: Chlorinated Diphenyl Oxide S119

Sampling and Analysis

Test Level		Found		
		µg	Liters	mg/cu m*
0.5S		8.64	89.3	0.0968
		8.80	87.7	0.1003
		8.47	89.3	0.0948
		9.59	87.7	0.1094
		8.84	86.8	0.1018
		8.63	88.0	0.0981
			n = 6	
			mean	0.1002
			std dev	0.005
			CV_2	0.050
1S		33.2	93.0	0.357
		37.6	91.0	0.413
		37.2	90.4	0.412
		37.9	91.6	0.414
		37.1	91.3	0.406
		36.2	91.3	0.396
			n = 6	
			mean	0.400
			std dev	0.022
			CV_2	0.055
2S		89.3	89.7	0.996
		89.3	88.0	1.015
		85.4	87.2	0.979
		81.4	87.8	0.927
		82.1	88.4	0.929
		83.1	88.1	0.943
			n = 6	
			mean	0.965
			std dev	0.037
$\overline{CV}_2$	0.048		CV_2	0.038

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Chlorodiphenyl (54% Chlorine), No. S121
OSHA Standard:	0.5 mg/cu m
Chemical used for validation:	Chlorodiphenyl (54% Chlorine) Monsanto

Procedure

The general procedure used is described in NIOSH Method No. S121 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for gas chromatographic analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 100-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot (5, 10, and 20 microliters) of a 0.0125 mg/μl solution of chlorodiphenyl (54% chlorine) in petroleum ether was added to 37-mm type AA Millipore filters. Chlorodiphenyl (54% chlorine) was extracted from the filter with petroleum ether and analyzed in a Varian 1800 Gas Chromatograph with a Nickel-63 electron capture detector. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. The area of the envelope of peaks eluting between approximately 80 seconds and 7 minutes was measured. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S121.

Test atmospheres of chlorodiphenyl (54% chlorine) at concentrations at 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on the Millipore filters in open-faced filter cassettes. The results of analysis of these samples are given in the Sampling and Analysis table. The estimated average size of the particles was 1 micron diameter. The collection efficiency at 2X the OSHA standard was measured for material which might have passed through the first filter. The collection efficiency was found to be 0.976 ± 0.002.

Modification

The method used for Sampling and Analysis was a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for gas chromatographic analysis of organic samples.

Generation

Samples of chlorodiphenyl (54% chlorine) in air were generated by the procedure described in Reference No. 1.

A 0.25% solution of chlorodiphenyl (54% chlorine) in toluene (2.5 g of chlorodiphenyl (54% chlorine) made up to a 1-liter volume with toluene) was used in the aspiration system. Samples of chlorodiphenyl (54% chlorine) were generated and collected separately at each of three levels, 0.5X, 1X, and 2X the OSHA standard.

The output of the aspirator was diluted with air at a rate of 111.5 liters/minute to get the 2X level. A lower aspirator output was diluted by 295 liters/minute and 420 liters/minute to get the 1X and 0.5X levels, respectively.

Samples were collected and analyzed to monitor the concentration in the sampling chamber at each of the three levels. When the desired concentration was reached, six samples at each level were collected. Samples were collected for 68 minutes at a rate of approximately 1.5 liters/minute in closed faced filter cassettes. The collection efficiency of chlorodiphenyl (54% chlorine) was found to be 0.976 $\pm$ 0.002. The collection efficiency was used as a correction factor to determine the concentration of air to compensate for any bias in the method.

Collection Efficiency

The concentration of chlorodiphenyl (54% chlorine) could not be measured directly with either the gas chromatograph or the total hydrocarbon analyzer because the concentration was too low. Collection efficiency was determined by measuring the amount of particulates collected on each of two filters mounted back-to-back. The collection efficiency of the filter was found to be 0.976 $\pm$ 0.002.

Analytical method recoveries at 0.1X the OSHA standard level were done. The results are given in the following table.

mg taken	mg found	A.M.R.
0.00525	0.00509	0.970
0.00525	0.00478	0.910
0.00525	0.00493	0.939
	mean	0.940

The average analytical method recovery (0.940) was used as a correction factor in correcting the mg found in the backup filter during the collection efficiency experiments.

The collection efficiency experiment was done at a generated concentration of 1.255 mg/cu m. The results are given in the following table on the next page.

COLLECTION EFFICIENCY OF CHLORODIPHENYL (54% CHLORINE)

ON MILLIPORE FILTERS

mg on first filter	mg on back filter	corr. mg on back filter	Collection Efficiency (%)
0.1208	0.00275	0.00293	97.6
0.1246	0.00327	0.00348	97.3
0.1201	0.00256	0.00272	97.8
0.1242	0.00285	0.00303	97.6
0.1219	0.00266	0.00283	97.7
		mean	97.6
		std dev	0.2

Discussion

The stabilities of samples stored in filter cassette holders vs. screw cap bottles were tested. Six filters were spiked at the 1X OSHA standard level. Three filters were stored in the filter cassette holders and 3 in screw cap bottles. The samples were stored at room temperature for 5 days before analysis. The following table gives the results.

A.M.R. FOR SAMPLES OF CHLORODIPHENYL (54% CHLORINE)

STORED IN CASSETTE HOLDERS FOR FIVE DAYS

mg spiked	mg found	Recovery
0.0525	0.0402	0.766
0.0525	0.0387	0.737
0.0525	0.0417	0.794

A.M.R. FOR SAMPLES OF CHLORODIPHENYL (54% CHLORINE)

STORED IN SCREW CAP BOTTLES

mg spiked	mg found	Recovery
0.0525	0.0506	0.964
0.0525	0.0507	0.966
0.0525	0.0502	0.956

From the above results, it was decided that the exposed filters should be transferred to screw cap bottles within one hour after sample collection.

A great deal of expertise is required in order to get adequate results in the analytical method using a gas chromatograph with an electron capture detector.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.021$ $\overline{CV}_2 = 0.038$ $\overline{CV}_T = 0.063$

Data Sheet: Chlorodiphenyl (54% Chlorine), No. S121

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.0263	0.0247	0.939	0.0525	0.0492	0.937	0.1050	0.0999	0.951
0.0263	0.0251	0.954	0.0525	0.0500	0.952	0.1050	0.1051	1.001
0.0263	0.0237	0.901	0.0525	0.0500	0.952	0.1050	0.1042	0.992
0.0263	0.0245	0.932	0.0525	0.0488	0.930	0.1050	0.1028	0.979
0.0263	0.0251	0.954	0.0525	0.0487	0.928	0.1050	0.0981	0.934
0.0263	0.0250	0.951	0.0525	0.0498	0.949	0.1050	0.1000	0.952
n =		6			6			6
mean		0.938			0.941			0.968
std dev		0.020			0.011			0.026
CV_1		0.021			0.012			0.027

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{DE}}$ 0.023

An analytical method recovery of 0.950 was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Chlorodiphenyl (54% Chlorine), No. S121

Sampling and Analysis

Test Level	Found				
	mg	Corr mg	Liters	mg/cu m	Corr. mg/cu m*
0.5S	0.0298	0.0313	100.3	0.312	0.320
	0.0274	0.0288	100.7	0.286	0.293
	0.0318	0.0335	100.0	0.335	0.343
	0.0294	0.0309	99.2	0.311	0.319
	0.0308	0.0324	100.4	0.323	0.331
	0.0299	0.0315	99.6	0.316	0.324
				n = 6	
				mean	0.322
				std dev	0.017
				CV_2	0.053
1S	0.0494	0.0520	100.3	0.518	0.531
	0.0486	0.0512	100.7	0.508	0.520
	0.0510	0.0537	100.0	0.537	0.550
	0.0496	0.0522	99.2	0.526	0.539
	0.0475	0.0500	100.4	0.498	0.510
	0.0477	0.0502	99.6	0.504	0.516
				n = 6	
				mean	0.528
				std dev	0.015
				CV_2	0.028
2S	0.1148	0.1208	100.3	1.204	1.234
	0.1141	0.1201	100.7	1.193	1.222
	0.1158	0.1219	100.0	1.219	1.249
	0.1184	0.1246	99.2	1.256	1.287
	0.1180	0.1242	100.4	1.237	1.267
	0.0708	0.0745	99.6	0.748	0.766**
				n = 5	
				mean	1.252
				std dev	0.026
				CV_2	0.021

$\overline{CV}_2$ 0.038

* A collection efficiency of 97.6% was determined for chlorodiphenyl (54% chlorine). This was used to correct mg/cu m.

** Deleted as an outlier, because this value did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, o-Terphenyl, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Ethylene Dichloride (1,2-Dichloroethane), No. S122

OSHA Standard: 200 mg/cu m (T.W.A.)
405 mg/cu m (Ceiling)
810 mg/cu m (Peak - maximum duration of 5 minutes in any 3 hours)

Chemical used for validation: 1,2-Dichloroethane, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S122 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of ethylene dichloride represented in a 3-liter air sample. To minimize errors associated with volume measurements of less than 1 microliter, a solution of ethylene dichloride in carbon disulfide was used. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using octane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 81 mg/min of ethylene dichloride via a syringe injector to a dry air stream flowing at a rate of 0.0989 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 15 minutes (3.3 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 23.7 mg of ethylene dichloride when a test atmosphere containing 821 mg/cu m of ethylene dichloride in air was sampled at 0.187 liters per minute for 155 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data are based on a prior experiment.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for ethylene dichloride as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 17.41 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for ethylene dichloride show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0118 \qquad \overline{CV}_2 = 0.0607 \qquad \overline{CV}_T = 0.0788$$

The average recovery of the generated samples over all levels was

$$95.2 \pm 9.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Ethylene Dichloride S122

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.627	0.611	0.974	1.253	1.220	0.974	2.506	2.395	0.956
0.627	0.595	0.949	1.253	1.228	0.980	2.506	2.391	0.954
0.627	0.586	0.935	1.253	1.207	0.963	2.506	2.382	0.951
0.627	0.605	0.965	1.253	1.000*	0.798*	2.506	2.348	0.937
0.627	0.604	0.963	1.253	1.220	0.974	2.506	2.383	0.951
0.627	0.614	0.979	1.253	1.211	0.966	2.506	2.399	0.957
n =		6			5			6
mean		0.961			0.971			0.951
std dev		0.0164			0.00684			0.00729
CV_1		0.0171			0.00705			0.00767

$\overline{CV}_1$ 0.0118

$\overline{CV}_{A+\overline{DE}}$ 0.0128

*These values excluded from statistical analysis.

Data Sheet: Ethylene Dichloride, S122

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.611	0.636	3.38	188.2	195.3	
	0.626	0.652	3.38	192.9	195.3	
	0.640	0.667	3.38	197.3	195.3	
	0.603	0.628	3.38	185.8	195.3	
	0.627	0.653	3.38	193.2	195.3	
	0.626	0.652	3.38	192.9	195.3	
			n = 6			
			mean	191.7		98.2
			std dev	4.09		
			CV_2	0.0213		
1S	1.295	1.349	3.38	399	403	
	1.273	1.326	3.35	396	403	
	1.269	1.322	3.32	398	403	
	1.270	1.323	3.44	385	403	
	1.263	1.316	3.39	388	403	
	1.288	1.342	3.36	399	403	
			n = 6			
			mean	394		97.8
			std dev	6.11		
			CV_2	0.0155		
2S	2.125	2.214	3.48	636	819	
	2.607	2.716	3.39	801	819	
	2.620	2.729	3.39	805	819	
	2.183	2.274	3.38	673	819	
	2.360	2.458	3.51	700	819	
	2.594	2.702	3.39	797	819	
			n = 6			
			mean	735		89.7
			std dev	74.8		
			CV_2	0.1018		
			$\overline{CV}_2$	0.0607		

Backup Data Report

Substance:	1,1-Dichloroethane, No. S123
OSHA Standard:	100 ppm (405 mg/cu m)
Chemical used for validation:	1,1-Dichloroethane, Lot #120437 Aldrich Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,1-dichloroethane in air is described in NIOSH Method S123, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid 1,1-dichloroethane to represent 10-liter air samples. Samples of 1,1-dichloroethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,1-dichloroethane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.7 minutes). The "true" concentrations of 1,1-dichloroethane in the generated samples were determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of 1,1-dichloroethane in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions
for
1,1-Dichloroethane

Nitrogen flow rate	0.086 liter/minute at 22°C
Dilution air flow rate	42 liters/minute at 22°C
Bath temperature	0°C

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 1). The three sampling chambers were monitored alternately during sample collection. Samples were collected for 54.7 minutes at a rate of approximately 0.2 liter per minute(individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene Reference No. 1). Breakthrough occurred in 99 minutes when a concentration of 838 mg/cu m was sampled at a rate of 0.185 liter per minute.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.011$ $\overline{CV}_2 = 0.026$ $\overline{CV}_T = 0.057$

The average recovery at the OSHA standard level was 103.6%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: 1,1-Dichloroethane, S123

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.882	1.917	1.019	4.00	3.95	0.988	8.00	8.22	1.028
1.882	1.908	1.014	4.00	4.02	1.005	8.00	8.16	1.020
1.882	1.902	1.011	4.00	4.06	1.015	8.00	8.14	1.018
1.882	1.900	1.010	4.00	3.94	0.985	8.00	8.11	1.014
1.882	1.894	1.006	4.00	3.99	0.998	8.00	8.18	1.022
1.882	1.865	0.991	4.00	4.00	1.000	8.00	7.95	0.994
n =		6			6			6
mean		1.008			0.998			1.016
std dev		0.010			0.011			0.012
CV_1		0.010			0.011			0.012

$\overline{CV}_1$ 0.011

$\overline{CV}_{A+\overline{DE}}$ 0.012

The equation D.E. = $1.008 - e^{-6.15 \times \text{mg found}}$ was used to calculate the corr mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 4.

Data Sheet: 1,1-Dichloroethane, S123

Sampling and Analysis

Test Level	Found mg	Found Corr mg	Found Liters	Found mg/cu m*	Taken mg/cu m	Recovery
0.5S	2.182	2.165	10.45	207.2	211.9	
	2.544	2.524	11.38	221.8	211.9	
	2.255	2.237	10.28	217.6	211.9	
	2.472	2.452	10.99	223.1	211.9	
	2.289	2.271	10.83	209.7	211.9	
	2.339	2.320	10.50	221.0	211.9	
			n = 6			
			mean	216.7		102.3
			std dev	6.7		
			CV_2	0.031		
1S	3.71	3.68	8.59	428	421	
	3.98	3.95	8.97	440	421	
	4.22	4.19	9.57	438	421	
	4.18	4.15	9.57	434	421	
	4.11	4.08	9.13	447	421	
	4.24	4.21	9.74	432	421	
			n = 6			
			mean	436		103.6
			std dev	7		
			CV_2	0.016		
2S	8.28	8.21	9.96	824	838	
	8.87	8.80	10.17	865	838	
	9.06	8.99	10.12	888	838	
	8.51	8.44	10.12	834	838	
	8.83	8.76	10.12	866	838	
	8.76	8.69	10.28	845	838	
			n = 6			
			mean	854		101.9
			std dev	24		
$\overline{CV}_2$	0.026		CV_2	0.028		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	1,1,2,2-Tetrachloroethane, No. S124
OSHA Standard:	5 ppm (35 mg/cu m)
Chemical used for validation:	1,1,2,2-Tetrachloroethane, Lot 440 8541 J.T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,1,2,2-tetrachloroethane in air is described in NIOSH Method S124, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid 1,1,2,2-tetrachloroethane to represent 10-liter air samples. Samples of 1,1,2,2-tetrachloroethane in air were generated and collected on petroleum - based charcoal, Lot 104, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,1,2,2-tetrachloroethane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.7 minutes). The "true" concentrations of 1,1,2,2-tetrachloroethane were determined by comparison with a "bag" standard, using a gas chromatograph to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There were two major modifications to P&CAM 127.

Charcoal Lot 104 from SKC, Inc. was used instead of charcoal Lot 105. (See Discussion Section.)

It was also necessary to use a hexane solution of 1,1,2,2-tetrachloroethane containing 79.8 mg/ml to apply the analyte to the charcoal for desorption efficiency tests. This was done so it would not be necessary to inject less than 2 microliters at the 0.5X level.

Generation

Samples of 1,1,2,2-tetrachloroethane in air were generated by the procedure described in the Backup Data Report for 2-butoxy ethanol (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions
for
1,1,2,2-Tetrachloroethane

Nitrogen flow rate	0.126 liter/minute at 21.5°C
Dilution air flow rate	65.4 liters/minute at 21.5°C
Bath temperature	21.5°C

A gas chromatograph was used to monitor the generated vapor concentrations (Reference No. 1). Samples were collected for 54.7 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-Butanone (Reference No. 3). Less than 5% of the generated concentration of 101 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.185 liter/minute indicating a capacity of at least 4.5 mg of 1,1,2,2-tetrachloroethane in the charcoal tube.

Discussion

Desorption efficiency tests for 1,1,2,2-tetrachloroethane were run at 1X the OSHA standard using charcoal Lot 105 from SKC, Inc. Carbon disulfide and methylene chloride were used as desorbing solvents. The results are given below in the following table:

Desorption Efficiency Tests Using Charcoal Lot 105

mg taken	mg found	D.E.	Solvent
0.3190	0.2214	0.694	Carbon disulfide
0.3190	0.2257	0.708	Carbon disulfide
0.3190	0.2332	0.731	Carbon disulfide
0.3190	0.1890	0.592	Methylene chloride

Because of the low recoveries in the D.E. tests using charcoal Lot 105, charcoal Lot 104 from SKC, Inc. was tried. Using charcoal Lot 104 and carbon disulfide as the desorbing solvent, an average D.E. of 0.870 at 1X the OSHA standard was found. The results using charcoal Lot 104 can be found in the Sampling and Analysis table of this report.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.019$ $\overline{CV}_2 = 0.027$ $\overline{CV}_T = 0.057$

The average recovery at the OSHA standard level was 105.6%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: 1,1,2,2-Tetrachloroethane, S124

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.1595	0.1307	0.819	0.3190	0.2775	0.870	0.638	0.553	0.867
0.1595	0.1307	0.819	0.3190	0.2646	0.829	0.638	0.552	0.865
0.1595	0.1342	0.841	0.3190	0.2802	0.878	0.638	0.558	0.875
0.1595	0.1351	0.847	0.3190	0.2840	0.890	0.638	0.562	0.881
0.1595	0.1340	0.840	0.3190	0.2803	0.879	0.638	0.559	0.876
0.1595	0.1313	0.823	0.3190	0.2784	0.873	0.638	0.572	0.897
n =		6			6			6
mean		0.832			0.870			0.877
std dev		0.013			0.021			0.012
CV_1		0.016			0.024			0.014

$\overline{CV}_1$ 0.019

$\overline{CV}_{A+\overline{DE}}$ 0.021

The equation D.E. = $0.874 - e^{-23.6 \times \text{mg found}}$ was used to calculate the corr mg in the sampling and analysis table. A program for the use of this equation is documented in Reference No. 5.

Data Sheet: 1,1,2,2-Tetrachloroethane, S124

Sampling and Analysis

Test Level	Found mg	Found Corr mg	Found Liters	Found mg/cu m*	Taken mg/cu m	Recovery
0.5S	0.1602	0.1880	10.99	17.11	16.14	
	0.1626	0.1906	10.83	17.60	16.14	
	0.1587	0.1865	10.50	17.76	16.14	
	0.1542	0.1818	10.28	17.68	16.14	
	0.1737	0.2024	11.38	17.79	16.14	
	0.1551	0.1827	10.45	17.48	16.14	
			n = 6			
			mean	17.57		108.9
			std dev	0.25		
			CV_2	0.014		
1S	0.2659	0.3046	8.97	34.0	32.3	
	0.2436	0.2797	8.59	32.6	32.3	
	0.2874	0.3292	9.57	34.4	32.3	
	0.2888	0.3308	9.57	34.6	32.3	
	0.2829	0.3241	9.13	35.5	32.3	
	0.2855	0.3270	9.74	33.6	32.3	
			n = 6			
			mean	34.1		105.6
			std dev	1.0		
			CV_2	0.029		
2S	0.647	0.740	10.12	73.1	70.3	
	0.627	0.717	10.28	69.7	70.3	
	0.662	0.757	10.12	74.8	70.3	
	0.643	0.736	9.96	73.9	70.3	
	0.680	0.778	10.12	76.9	70.3	
	0.676	0.773	10.17	76.0	70.3	
			n = 6			
			mean	74.1		105.4
			std dev	2.5		
$\overline{CV}_2$	0.027		CV_2	0.034		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, 2-Butoxy ethanol, No. S76, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Trifluoromonobromomethane, No. S125
OSHA Standard:	1000 ppm (6090 mg/cu m)
Chemical used for validation:	Trifluoromonobromomethane Matheson Gas Products

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of trifluoromonobromomethane in air is described in NIOSH Method S125, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking large charcoal tubes with the appropriate amounts of trifluoromonobromomethane to represent 1-liter air samples. Samples of trifluoromonobromomethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with methylene chloride and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of trifluoromonobromomethane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 21.7 minutes). The "true" concentrations of trifluoromonobromomethane at 2X the OSHA standard in the generated samples were determined by using the flow rate of the effluent from the trifluoromonobromomethane gas cylinder and the dilution air flow rate. Known dilution factors were applied to determine the "true" concentration at the 1X and 0.5X OSHA standard levels. The generated concentrations at each level were also monitored using a total hydrocarbon analyzer, standardized by "bag" standards.

Modifications

There were two major modifications to P&CAM 127.

Methylene chloride, instead of carbon disulfide, was used as the desorbing solvent for the method. (See Discussion Section)

Large charcoal tubes from SKC, Inc. (9 cm long with a 8-mm O.D. and 6-mm I.D.) were used to collect the trifluoromonobromomethane. A smaller charcoal tube (7 cm long with a 6-mm O.D. and a 4-mm I.D.) is connected in line to the large charcoal tube as a back-up tube. (See Discussion Section)

Generation

Samples of trifluoromonobromomethane in air were generated by mixing a stream of pure trifluoromonobromomethane with air. Trifluoromonobromomethane was metered from a gas cylinder at a rate of 0.108 liter per minute. The effluent of the gas cylinder was diluted with air at a

rate of 56.79 liters per minute to obtain a concentration of 11,560 mg/cu m in the 2X chamber. Further dilutions were made to obtain the appropriate concentrations at the 1X and 0.5X OSHA standards. The samples were collected on large charcoal tubes (Charcoal Lot 105, 400 mg in the front section and 200 mg in the backup section), using the total tube for the sample. A smaller backup charcoal tube was connected in line to the larger sample tube with Tygon tubing. Samples were collected for 21.7 minutes at a rate of approximately 0.050 liter per minute (the flow rates vary slightly through individual critical orifices).

Breakthrough

A test for breakthrough on the large charcoal tube (400 mg of charcoal in the front section and 200 mg of charcoal in the back section) was made as described in the Backup Data Report for Cyclohexene (Reference No. 1). A total hydrocarbon analyzer was used to monitor the concentration of the analyte during the breakthrough test. Breakthrough occurred in 90 minutes when a concentration of 12,370 mg/cu m was sampled at a rate of 0.046 liter per minute.

Discussion

The GC conditions used with a 4-ft X 1/4-in stainless steel column packed with 50/80 mesh Porapak Q were as follows:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 170°C injector temperature
5. 230°C detector temperature
6. 105°C column temperature

It was necessary to choose another desorbing solvent for the method, because carbon disulfide gave a peak that interferred with the trifluoromonobromomethane peak on the gas chromatogram.

Methanol was tried, but trifluoromonobromomethane was not soluble in this solvent. Methylene chloride was tested, and the analyte was soluble in this solvent. The methylene chloride peak did not interfere with the trifluoromonobromomethane peak on the gas chromatogram. Methylene chloride was therefore chosen as the eluent for the method.

Large charcoal tubes from SKC, Inc., containing 400 mg of charcoal Lot 105 in the front section of the tube and 200 mg in the back section, were used to collect the trifluoromonobromomethane samples. It was necessary to use these large charcoal tubes, because breakthrough occurs in approximately 5 minutes with the smaller charcoal tubes (100 mg of charcoal Lot 105 in the front section of the tube and 50 mg in the back section). It was therefore decided to try the larger charcoal tubes to obtain a longer sampling time, and these tubes worked satisfactorily.

Preliminary experiments with the large charcoal tubes were done to test if trifluoromonobromomethane would migrate from the front section to the back section of the charcoal tube. Experiments at 1X the OSHA standard level were conducted by spiking three large charcoal tubes on one day and three tubes five days later. The following day both front and back sections of the six charcoal tubes were analyzed. The tubes that were spiked earlier showed evidence of the analyte migrating. Therefore, it was decided that it would be necessary to use a backup tube which could be stored separately from the collection tube. A smaller charcoal tube (containing 100 mg of charcoal in the front section and 50 mg in the back section) was connected in line to the larger tube as a backup tube during sample collection.

From the migration experiments, it was found that spiking for desorption efficiency tests should be done on the front section of the tubes, and both front and backup sections of the charcoal tube should be analyzed. The charcoal tubes were spiked in the following manner. A known amount of analyte was injected through a septum into nitrogen at a flow of approximately 200 ml/min. The resulting mixture of trifluoromonobromomethane and nitrogen was introduced into a charcoal tube.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.037$ $\overline{CV}_2 = 0.038$ $\overline{CV}_T = 0.065$

The average recovery at the OSHA standard level was 100%.

Data Sheet: Trifluoromonobromomethane, S125

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
3.05	2.57	0.843	6.09	4.92	0.808	12.18	9.56	0.785
3.05	2.71	0.889	6.09	4.96	0.814	12.18	9.80	0.805
3.05	2.47	0.810	6.09	5.18	0.851	12.18	9.84	0.808
3.05	2.54	0.833	6.09	4.64	0.762	12.18	9.74	0.800
3.05	2.40	0.787	6.09	4.82	0.791	12.18	9.52	0.782
3.05	2.43	0.797	6.09	4.90	0.805	12.18	9.08	0.745
n =		6			6			6
mean		0.826			0.805			0.788
std dev		0.037			0.029			0.023
CV_1		0.045			0.036			0.029

$\overline{CV}_1$ 0.037

$\overline{CV}_{A+\overline{DE}}$ 0.040

The equation D.E. = $0.806 - e^{-11.3 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 3.

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Data Sheet: Trifluoromonobromomethane, S125

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	2.409	2.989	1.031	2899	2890	
	2.336	2.898	1.001	2895	2890	
	2.483	3.081	1.023	3012	2890	
	2.260	2.804	1.003	2796	2890	
	2.286	2.836	1.027	2761	2890	
	2.147	2.664	0.999	2667	2890	
			n = 6			
			mean	2838		98.2
			std dev	122		
			CV_2	0.043		
1S	4.57	5.67	1.008	5620	5780	
	4.62	5.73	1.003	5710	5780	
	4.44	5.51	1.005	5480	5780	
	4.64	5.76	1.005	5730	5780	
	4.96	6.15	0.990	6210	5780	
	4.77	5.92	0.999	5930	5780	
			n = 6			
			mean	5780		100.0
			std dev	260		
			CV_2	0.045		
2S	8.44	10.47	0.992	10550	11500	
	8.48	10.52	0.990	10630	11500	
	8.48	10.52	0.992	10600	11500	
	8.62	10.69	0.986	10840	11500	
	8.55	10.61	1.016	10440	11500	
	(Sample was lost.)					
			n = 5			
			mean	10610		92.3
			std dev	150		
$\overline{CV}_2$ 0.038			CV_2	0.014		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	1,2,3-Trichloropropane, No. S126
OSHA Standard:	50 ppm (300 mg/cu m)
Chemical used for validation:	1,2,3-Trichloropropane, Lot #082051 Aldrich Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,2,3-trichloropropane in air is described in NIOSH Method S126, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid 1,2,3-trichloropropane to represent 10-liter air samples. Samples of 1,2,3-trichloropropane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,2,3-trichloropropane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.7 minutes). The "true" concentrations of 1,2,3-trichloropropane in the generated samples were determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of 1,2,3-trichloropropane in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions
for
1,2,3-Trichloropropane

Nitrogen flow rate	0.727 liter/minute at 21°C
Dilution air flow rate	37.0 liters/minute at 21°C
Bath temperature	30°C

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A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 1). The three sampling chambers were monitored alternately during sample collection. Samples were collected for 54.7 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 1). Less than 5% of the generated concentration of 629 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.185 liter per minute, indicating a capacity of at least 28 mg of 1,2,3-trichloropropane in the charcoal tube.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.027$ $\overline{CV}_2 = 0.045$ $\overline{CV}_T = 0.068$

The average recovery at the OSHA standard level was 108.2%. However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: 1,2,3-Trichloropropane, S126

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.528	1.407	0.921	3.06	2.894	0.946	6.11	5.84	0.956
1.528	1.513	0.990	3.06	2.842	0.929	6.11	5.86	0.959
1.528	1.465	0.959	3.06	2.982	0.974	6.11	6.02	0.985
1.528	1.469	0.961	3.06	2.900	0.948	6.11	5.68	0.930
1.528	1.490	0.975	3.06	2.911	0.951	6.11	5.45	0.892
1.528	1.502	0.983	3.06	2.835	0.926	6.11	5.94	0.972
n =		6			6			6
mean		0.965			0.946			0.949
std dev		0.025			0.017			0.033
CV_1		0.026			0.018			0.035

$\overline{CV}_1$ 0.027

$\overline{CV}_{A+\overline{DE}}$ 0.029

The equation D.E. = $0.953 - e^{-93.5 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 4.

Data Sheet: 1,2,3-Trichloropropane, S126

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	1.670	1.752	10.71	163.6	163.0	
	1.650	1.731	11.09	156.1	163.0	
	1.783	1.871	10.18	183.8	163.0	
	1.720	1.805	10.23	176.4	163.0	
	1.671	1.753	10.55	166.2	163.0	
	1.516	1.591	10.02	158.8	163.0	
			n = 6			
			mean	167.5		102.8
			std dev	10.7		
			CV_2	0.064		
1S	2.817	2.956	8.97	330	303	
	2.655	2.786	8.42	331	303	
	2.862	3.003	9.08	331	303	
	3.023	3.172	9.57	331	303	
	2.722	2.856	9.24	309	303	
	3.064	3.215	9.57	336	303	
			n = 6			
			mean	328		108.2
			std dev	10		
			CV_2	0.030		
2S	5.98	6.27	10.12	620	629	
	6.07	6.37	10.28	620	629	
	5.69	5.97	10.12	590	629	
	5.43	5.70	9.96	572	629	
	5.68	5.96	10.17	586	629	
	5.86	6.15	10.12	608	629	
			n = 6			
			mean	599		95.2
			std dev	20		
$\overline{CV}_2$	0.045		CV_2	0.033		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Trichloronaphthalene, No. S128
OSHA Standard:	5 mg/cu m - skin
Chemical Used for Validation:	Trichloronaphthalene Koppers

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method S128. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 100-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of a 1.25 g/10 ml solution of trichloronaphthalene in benzene was spiked onto 37-mm glass fiber filters. The analyte was extracted from the filters with 15 ml of iso-octane and analyzed by gas chromatography with an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S128.

Test atmospheres of trichloronaphthalene at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type A glass fiber filters connected in series with a midget bubbler containing 15 ml of iso-octane.

Generation

Samples of trichloronaphthalene were generated by the procedure described in Reference No. 1. A solution of trichloronaphthalene in toluene (10 g/liter) was used in the aspiration system. A pressure drop of 20 psi across the aspirator tip was used in the generation. The output of the aspirator was diluted with air at a flow rate of 321.1 liters/minute to obtain the 2X concentration level. The Thermo-Systems Model 3200 particle mass monitor was used to determine the amount of dilution air needed to dilute the aspirator output to obtain a concentration at approximately the 2X level. It was also used to establish the proper flow rates in the secondary dilution system to achieve the serial dilutions to the 1X and 0.5X levels. This is necessary, because in the process of diluting the aerosol to the 1X and 0.5X levels, there is loss of particles on the walls of the sample rationing system. The particle mass monitor system is described in the Attachment Section of this report.

The dilution system is described in Reference No. 2.

Samples were collected for 81.7 minutes at a flow rate of approximately 1.3 liters/minute.

Collection Efficiency

Collection efficiency was determined at a concentration of 8.79 mg/cu m by connecting a filter and two midget bubblers (each containing 15 ml of iso-octane) in series. This collection efficiency test was done on the six samples used for validation at 2X the OSHA standard. Samples were collected for 81.7 minutes at a flow rate of 1.3 liters/minute. The collection efficiency of the single filter and bubbler was determined to be 1.00 since no trichloronaphthalene was detected in the second bubbler at a detection limit of 0.018 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below.

Total Concentration found in the filter & first bubbler	Concentration found in second bubbler	Collection Efficiency
8.00 mg/cu m	N.D.*	1.00
10.91 " " "	"	"
8.61 " " "	"	"
8.47 " " "	"	"
7.72 " " "	"	"
9.01 " " "	"	"

* N.D. = Not detected at a detection limit of 0.01 mg/cu m.

Discussion

It was decided to collect trichloronaphthalene using a 37-mm glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane, because it was expected that trichloronaphthalene would exist partly as a particulate and partly as a vapor. No experimental work was done to test this, but experimental work on collection of pentachloronaphthalene was conducted (Reference No. 3). It was found that pentachloronaphthalene was collected most efficiently using a glass fiber filter connected in series to a midget bubbler. Trichloronaphthalene was expected to behave in a similar manner, and therefore, the same collection method was used.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for trichloronaphthalene as in Reference No. 5.

The sampling and analysis data gave a chi squared value of 10.72 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. Therefore, CV_T is calculated only on the data at the 1X level.

$$CV_T = \sqrt{CV_2^2 + (0.05)^2} = 0.117$$

Where:

CV_2 = Coefficient of Variation (Sampling and Analysis) at the 1X level = 0.106

(0.05) = pump error

Data Sheet: Trichloronaphthalene S128

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
250	229	0.916	500	424	0.848	1000	1040	1.040
250	231	0.924	500	486	0.972	1000	992	0.992
250	202	0.808	500	499	0.998	1000	1028	1.028
250	217	0.868	500	501	1.002	1000	1006	1.006
250	236	0.944	500	521	1.042	1000	977	0.977
250	249	0.996	500	504	1.008	1000	986	0.986
n =		6			6			6
mean		0.909			0.978			1.005
std dev		0.065			0.068			0.025
CV_1		0.072			0.070			0.025

$\overline{CV}_1$ 0.060

$\overline{CV}_{A+\overline{AMR}}$ 0.065

The average Analytical Method Recovery (A.M.R.) at each level was used to calculate corr. µg in the Sampling and Analysis Table.

Data Sheet: Trichloronaphthalene S128

Sampling and Analysis

Test Level	Found			
	µg	Corr µg	Liters	mg/cu m*
0.5S	151.2	166.3	99.6	1.670
	154.0	169.4	104.5	1.621
	154.9	170.4	101.2	1.684
	147.1	161.8	101.2	1.599
	155.2	170.7	102.0	1.674
	157.8	173.6	106.1	1.636
			n = 6	
			mean	1.647
			std dev	0.034
			CV_2	0.021
1S	442	452	102.8	4.40
	424	434	97.9	4.43
	446	456	102.8	4.44
	472	483	84.9	5.69
	473	484	102.0	4.75
	426	436	97.1	4.49
			n = 6	
			mean	4.70
			std dev	0.50
			CV_2	0.106
2S	778	774	96.8	8.00
	928	923	84.6	10.91
	886	882	102.4	8.61
	831	827	97.6	8.47
	795	791	102.4	7.72
	920	915	101.6	9.01
			n = 6	
			mean	8.79
			std dev	1.14
			CV_2	0.130

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Pentachloronaphthalene, No. S92, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Attachment to Trichloronaphthalene Backup Data Report

Use of the Particle Mass Monitor in Particulate Generation

Introduction

The Thermo-Systems Inc. Model 3200A particle mass monitor is designed for automatic measurement of total airborne particles (μg/cu m). Measurements are very fast and reproducible. Airborne particles ranging in size from 0.01 to 20 microns in diameter are sampled with a vacuum supply and are collected on a quartz crystal sensor with an electrostatic precipitator collector. The mass of particles is then electronically weighed by the sensor. The output of the particle mass monitor (a frequency signal) is monitored with a digital counter. Frequency differences are proportional to the mass deposited.

Principle of Operation

The particle mass monitor includes the following: the electrostatic-precipitator chamber, sensors, oscillator and mixed circuitry, and power supplies.

The aerosol to be sampled is drawn into the electrostatic-precipitator chamber at a flow rate of 1 liter/minute using an external vacuum supply.

Specifications

Mass Concentration:	1 - 20,000 μg/cu m
Size Range (diameter):	0.01 to 20 microns
Sensitivity:	180 Hz/μg
Resolution:	± 1 Hz or ± 0.006 μg
Sample Flow Rate:	1 liter/minute
Maximum Sensor Loading:	40 μg

Use in Generation of Particulates

The particle mass monitor is used to establish three sets of generator conditions for the generation of particulate samples:

1. Establish generation conditions to yield a 2X level concentration in the primary sampling chamber.

2. Determine the appropriate dilution air flow rates to achieve dilutions to the 1X and 0.5X OSHA levels.

3. Monitor the output of the generator (to assure constancy) during sample collection.

The aerosol generation system is attached to the three-stage dilution system, and the particle mass monitor is attached to the 2X sampling chamber. All of the particles in the air stream are deposited onto the surface of the sensor with an electrostatic-precipitator collector.

The sensor is a piezoelectric quartz crystal oscillating at its resonance frequency. It is driven by a solid-state oscillator circuit. The resonant frequency of the quartz crystal decreases linearity with the total mass of the particulate deposition, automatically weighing the airborne particles. A second sensor (the reference crystal) compensates for changes in ambient effects, such as temperature and gas composition.

The frequency output of the primary, or measuring, crystal and the reference crystal are subtracted in a solid-state mixer circuit. The time rate-of-change of the output frequency signal is directly proportional to the total particle mass concentration, C, in the range of 0.01 to 20 microns.

$$C = 333 \, \Delta F / \Delta t$$

where

C = the concentration in μg/cu m
ΔF = frequency shift (Hz)
Δt = sampling time (seconds)

The measuring crystal is cleaned by washing with acetone and methyl alcohol and allowed to air dry. The clean crystal is weighed and placed in the electrostatic-precipitator chamber. The 2X chamber is sampled at a flow rate of 1.0 liter/minute for 10-15 minutes. During sampling, counter/time is used to determine the frequency shift between the reference and measuring crystals. The frequency shift, ΔF, and the sampling time, Δt, are then used to calculate the concentration in the chamber. The measuring crystal is removed from the precipitator chamber and weighed. From the weight of the crystal, sampling time and sampling flow rate, the approximate concentration in the 2X level chamber may be calculated. The comparison of theoretical and measured concentrations is important to show proper functioning of the equipment and also compensate for deterioration of the crystal with age (i.e., the frequency shift for the matched crystals, when both are clean, will increase with age and wear).

To determine the proper dilution air flow rates to achieve the 1X and 0.5X levels, the same procedure, as previously described, is used except that sampling is done at the 1X and 0.5X chambers.

Once the three concentration levels have been selected, the particle mass monitor is attached to the 2X chamber, and sample collection

is begun. During the collection of the samples, the particle mass monitor is used periodically to check the constancy of the generator.

Another application of the particle mass monitor is its use in the determination of possible loss of organic particulate from a filter due to vaporization. If a substance has a significant vapor pressure, particulate matter would vaporize off of the crystal, resulting in a decrease in the frequency shift shown on the counter/time.

Backup Data Report

Substance:	1,1,2-Trichloro-1,2,2-trifluoroethane, No. S129
OSHA Standard:	1000 ppm (7660 mg/cu m)
Chemical used for validation:	1,1,2-Trichloro-1,2,2-trifluoroethane Matheson Gas Products

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,1,2-trichloro-1,2,2-trifluoroethane in air is described in NIOSH Method S129, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid 1,1,2-trichloro-1,2,2-trifluoroethane to represent 1.5-liter air samples. Samples of 1,1,2-trichloro-1,2,2-trifluoroethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,1,2-trichloro-1,2,2-trifluoroethane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 32.6 minutes). The "true" concentrations of 1,1,2-trichloro-1,2,2-trifluoroethane in the generated samples were determined by comparison with a "bag" standard, using a gas chromatograph to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of 1,1,2-trichloro-1,2,2-trifluoroethane in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions
for
1,1,2-Trichloro-1,2,2-trifluoroethane

Nitrogen flow rate	0.32 liter/minute at 22°C
Dilution air flow rate	18.8 liters/minute at 22°C
Bath temperature	0°C

A gas chromatograph was used to monitor the generated vapor concentrations (Reference No. 1). The three sampling chambers were monitored alternately during sample collection. Samples were collected for 32.6 minutes at a rate of approximately 0.050 liter per minute (individual critical oridices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-Butanone (Reference No. 3). Breakthrough occurred in 60 minutes when a concentration of 14,500 mg/cu m was sampled at a rate of 0.046 liter per minute.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.020$ $\overline{CV}_2 = 0.048$ $\overline{CV}_T = 0.070$

The average recovery at the OSHA standard level was 100.3%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: 1,1,2-Trichloro-1,2,2-trifluoroethane, S129

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
5.63	5.80	1.030	11.42	11.35	0.994	22.83	22.52	0.986
5.63	6.00	1.066	11.42	11.88	1.040	22.83	22.40	0.981
5.63	5.72	1.016	11.42	11.70	1.025	22.83	23.25	1.018
5.63	5.72	1.016	11.42	11.50	1.007	22.83	22.21	0.973
5.63	5.91	1.050	11.42	11.17	0.978	22.83	22.69	0.994
5.63	5.83	1.036	11.42	11.38	0.996	22.83	22.80	0.999
n =		6			6			6
mean		1.036			1.007			0.992
std dev		0.020			0.023			0.016
CV_1		0.019			0.023			0.016

$\overline{CV}_1$ 0.020

$\overline{CV}_{A+\overline{DE}}$ 0.022

The equation D.E. = 1.011 - $e^{-8.62 \times \text{mg found}}$ was used to calculate the corr mg in the sampling and analysis table. A program for the use of this equation is documented in Reference No. 5.

Data Sheet: 1,1,2-Trichloro-1,2,2-trifluoroethane, S129

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	5.28	5.22	1.539	3392	3300	
	4.50	4.45	1.509	2949	3300	
	4.94	4.89	1.506	3247	3300	
	5.04	4.99	1.545	3230	3300	
	4.72	4.67	1.552	3009	3300	
	(Sample was lost because of a bad orifice)					
			n = 5			
			mean	3165		95.9
			std dev	183		
			CV_2	0.058		
1S	11.02	10.90	1.513	7204	6870	
	10.82	10.70	1.509	7091	6870	
	9.96	9.85	1.503	6554	6870	
	10.59	10.48	1.513	6927	6870	
	9.71	9.60	1.490	6443	6870	
	10.93	10.81	1.516	7131	6870	
			n = 6			
			mean	6892		100.3
			std dev	320		
			CV_2	0.046		
2S	21.37	21.14	1.450	14,580	14,200	
	21.08	20.85	1.493	13,960	14,200	
	20.63	20.41	1.490	13,700	14,200	
	20.53	20.31	1.480	13,720	14,200	
	19.88	19.66	1.493	13,170	14,200	
	9.04	8.94	0.685	13,050	14,200	
			n = 6			
			mean	13,700		96.5
			std dev	556		
$\overline{CV}_2$	0.048		CV_2	0.041		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Tetrachloronapthalene, No. S130
OSHA Standard:	2 mg/cu m - skin
Chemical Used for Validation:	Tetrachloronaphthalene Koppers

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S130. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 100-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of a 50 mg/ml solution of tetrachloronaphthalene in benzene were spiked onto 37-mm glass fiber filters. The analyte was extracted from the filter with 15 ml iso-octane and analyzed by gas chromatography with an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S130.

Test atmospheres of tetrachloronaphthalene at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type A glass fiber filters connected in series with a midget bubbler containing 15 ml of iso-octane.

Generation

Samples of tetrachloronaphthalene were generated by the procedure described in Reference No. 1. A solution of tetrachloronaphthalene in toluene (10 g/liter) was used in the aspiration system. A pressure drop of 15 psi across the aspirator tip was used in the generation. The output of the aspirator was diluted with air at a flow rate of 321.1 liters/minute to obtain the 2X concentration level. The Thermo-Systems Model 3200 particle mass monitor was used to determine the amount of dilution air needed to dilute the aspirator output to obtain a concentration at approximately the 2X level. It was also used to establish the proper flow rates in the secondary dilution system to achieve the serial dilutions to the 1X and 0.5X levels. This is necessary, because in the process of diluting the aerosol to the 1X and 0.5X levels, there is loss of particles on the walls of the sample rationing system. The particle mass monitor system is described in the Attachment Section of Reference No. 2. The dilution system is described in Reference No. 3. Samples were collected for 81.3 minutes at a flow rate of approximately 1.3 liters/minute.

Collection Efficiency

Collection efficiency was determined at a concentration of 4.04 mg/cu m by connecting a filter and two midget bubblers (each containing 15 ml of iso-octane) in series. This collection efficiency test was done on six samples used for validation at 2X the OSHA standard. Samples were collected for 81.3 minutes at a flow rate of 1.3 liters per minute. The collection efficiency of the single filter and bubbler was determined to be 1.00, since no tetrachloronaphthalene was detected in the second bubbler at a detection limit of 0.010 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below.

Total mg/cu m found in the filter and first bubbler	mg/cu m found in second bubbler	Collection Efficiency
3.88	N.D.*	1.00
3.80	"	1.00
3.65	"	1.00
3.89	"	1.00
4.14	"	1.00
4.88	"	1.00

*N.D. = Not detected at a detection limit of 0.01 mg/cu m.

Discussion

It was decided to collect tetrachloronaphthalene using a 37-mm glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane, because it was expected that tetrachloronaphthalene would exist partly as particulate and partly as a vapor. No experimental work was done to test this, but experimental work on collection of pentachloronaphthalene was conducted (Reference No. 4). It was found that pentachloronaphthalene was collected most efficiently using a glass fiber filter connected in series to a midget bubbler. Tetrachloronaphthalene was expected to behave in a similar manner, and therefore, the same collection method was used.

Precision and Accuracy

The statistical procedures used are described in Reference No. 5.

$\overline{CV}_1 = 0.052$ $\overline{CV}_2 = 0.080$ $\overline{CV}_T = 0.097$

Data Sheet: Tetrachloronaphthalene S130

Analysis

Level	0.5S		1S			2S		
μg taken	μg found	A.M.R.	μg taken	μg found	A.M.R.	μg taken	μg found	A.M.R.
100.3	107.2	1.069	200.0	210.9	1.054	401	346	0.863
100.3	98.2	0.979	200.0	198.9	0.994	401	351	0.875
100.9	99.0	0.981	201.8	194.2	0.962	404	373	0.923
100.9	98.1	0.972	201.8	197.5	0.979	404	367	0.908
101.0	98.0	0.970	202.1	192.7	0.953	404	379	0.938
101.0	86.1	0.852	202.1	207.1	1.025	404	386	0.955
n =		6			6			6
mean		0.970			0.994			0.910
std dev		0.069			0.039			0.036
CV_1		0.071			0.039			0.040

$\overline{CV}_1$ 0.052

$\overline{CV}_{A+\overline{AMR}}$ 0.056

The average Analytical Method Recovery (A.M.R.) at each level was used to calculate the corr. mg in the Sampling and Analysis Table.

Data Sheet: Tetrachloronaphthalene S130

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.0923	0.0952	104.9	0.908
	0.0908	0.0936	98.4	0.951
	0.0902	0.0930	92.7	1.003
	0.0912	0.0940	104.1	0.903
	0.0776	0.0800	100.8	0.794
	Sample was lost.			
			n = 5	
			mean	0.912
			std dev	0.077
			CV_2	0.084
1S	0.1750	0.1761	105.7	1.666
	0.1677	0.1687	100.8	1.674
	0.1609	0.1619	101.6	1.594
	0.1653	0.1663	100.8	1.650
	0.1691	0.1701	99.2	1.715
	0.1739	0.1750	104.1	1.681
			n = 6	
			mean	1.663
			std dev	0.040
			CV_2	0.024
2S	0.345	0.379	97.6	3.88
	0.354	0.389	102.4	3.80
	0.321	0.353	96.8	3.65
	0.362	0.398	102.4	3.89
	0.383	0.421	101.6	4.14
	0.376	0.413	84.6	4.88
			n = 6	
			mean	4.04
			std dev	0.44
$\overline{CV}_2$ 0.080			CV_2	0.109

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Trichloronaphthalene, No. S128, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Pentachloronaphthalene, No. S92, prepared under NIOSH Contract CDC-99-74-45.

5. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	1,1,1,2-Tetrachloro-2,2-difluoroethane, No. S131
OSHA Standard:	500 ppm (4170 mg/cu m)
Chemical used for validation:	1,1,1,2-Tetrachloro-2,2-difluoroethane Chemicals Procurement Laboratories, Inc.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,1,1,2-tetrachloro-2,2-difluoroethane in air is described in NIOSH Method S131, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of solid 1,1,1,2-tetrachloro-2,2-difluoroethane in hexane to represent 2-liter air samples. Samples of 1,1,1,2-tetrachloro-2,2-difluoroethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,1,1,2-tetrachloro-2,2-difluoroethane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 43.5 minutes). The "true" concentrations of 1,1,1,2-tetrachloro-2,2-difluoroethane in the generated samples were determined by comparison with a "bag" standard, using a gas chromatograph to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There was one major modification to P&CAM 127. Since the analyte is a solid, it was necessary to dissolve the analyte in hexane for desorption efficiency tests. A hexane solution of the analyte containing 1336 mg/ml was used.

Generation

Samples of 1,1,1,2-tetrachloro-2,2-difluoroethane in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2). A heat lamp was used to heat the top section of the generator to about 100°C to melt any particulate that may be formed in this section. A glass wool plug was also used to remove any particulate that formed in the inlet of the diluting section of the vapor generator. The three sampling chambers were monitored alternately during sample collection. The generator conditions used are given in the following table:

Generator Conditions
for
1,1,1,2-Tetrachloro-2,2-difluoroethane

Nitrogen flow rate	0.294 liter/minute at 22°C
Dilution air flow rate	31.9 liters/minute at 22°C
Bath temperature	40°C

A gas chromatograph was used to monitor the generated vapor concentrations (Reference No. 1). Samples were collected for 43.5 minutes at a rate of approximately 0.050 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-butanone (Reference No. 3). Breakthrough occurred in 77 minutes when a concentration of 14,300 mg/cu m was sampled at a rate of 0.035 liter per minute.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for 1,1,1,2-tetrachloro-2,2-difluoroethane as in Reference No. 4.

The sampling and analysis data gave a chi squared value of 22.7 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for 1,1,1,2-tetrachloro-2,2-difluoroethane show excellent precision. Therefore, pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the data for the three levels.

The statistical procedures used are described in Reference No. 5.

$\overline{CV}_1 = 0.027 \quad \overline{CV}_2 = 0.046 \quad \overline{CV}_T = 0.069$

The average recovery at the OSHA standard level was 101.3%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: 1,1,1,2-Tetrachloro-2,2-difluoroethane, S131

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
4.14	4.76	1.150	8.28	8.68	1.048	16.57	16.96	1.024
4.14	4.38	1.058	8.28	8.69	1.050	16.57	16.58	1.001
4.14	4.25	1.027	8.28	8.67	1.047	16.57	16.77	1.012
4.14	4.45	1.075	8.28	8.69	1.050	16.57	16.84	1.016
4.14	4.36	1.053	8.28	8.77	1.059	16.57	16.55	0.999
4.14	4.18	1.010	8.28	8.67	1.047	16.57	16.81	1.014
n=		6			6			6
mean		1.062			1.050			1.011
std dev		0.049			0.005			0.009
CV_1		0.046			0.005			0.009

$\overline{CV}_1$ 0.027

$\overline{CV}_{A+\overline{DE}}$ 0.029

The equation D.E. = $1.041 - e^{-6.26 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 6.

Data Sheet: 1,1,1,2-Tetrachloro-2,2-difluoroethane, S131

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.73	4.54	2.013	2255	2160	
	4.76	4.57	2.060	2218	2160	
	4.82	4.63	2.069	2238	2160	
	4.69	4.51	2.004	2250	2160	
	4.97	4.77	2.052	2325	2160	
	(Sample was lost.)					
			n = 5			
			mean	2257		104.5
			std dev	40		
			CV_2	0.018		
1S	9.61	9.23	2.017	4580	4490	
	9.48	9.11	2.013	4530	4490	
	9.46	9.09	1.987	4570	4490	
	9.46	9.09	2.004	4540	4490	
	9.54	9.16	2.021	4530	4490	
	9.59	9.21	2.017	4570	4490	
			n = 6			
			mean	4550		101.3
			std dev	23		
			CV_2	0.005		
2S	19.06	18.31	1.978	9260	9020	
	8.10	7.78	0.856	9090	9020	
	13.12	12.60	1.165	10820	9020	
	18.56	17.83	1.987	8970	9020	
	18.98	18.23	1.974	9240	9020	
	8.94	8.59	2.039	4210*	9020	
			n = 5			
			mean	9480		105.1
			std dev	761		
$\overline{CV}_2$	0.046		CV_2	0.080		

* Deleted as an outlier, because this value did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 7.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

5. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

6. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W.J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

7. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	1,1,2,2-Tetrachloro-1,2-difluoroethane, No. S132
OSHA Standard:	500 ppm (4170 mg/cu m)
Chemical used for validation:	1,1,2,2-Tetrachloro-1,2-difluoroethane Chemicals Procurement Laboratories, Inc.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of 1,1,2,2-tetrachloro-1,2-difluoroethane in air is described in NIOSH Method S132, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of solid 1,1,2,2-tetrachloro-1,2-difluoroethane in hexane to represent 2-liter air samples. Samples of 1,1,2,2-tetrachloro-1,2-difluoroethane in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of 1,1,2,2-tetrachloro-1,2-difluoroethane in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 43.5 minutes). The "true" concentrations of 1,1,2,2-tetrachloro-1,2-difluoroethane in the generated samples were determined by comparison with a "bag" standard, using a gas chromatograph to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There was one major modification to P&CAM 127. Since the analyte is a solid, it was necessary to dissolve the analyte in hexane for desorption efficiency tests. A hexane solution of the analyte containing 861 mg/ml was used.

Generation

Samples of 1,1,2,2-tetrachloro-1,2-difluoroethane in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2). A heat lamp was used to heat the top section of the generator to about 100°C to melt any particulate that may be formed in this section. A glass wool plug was also used to remove any particulate that formed in the inlet of the diluting section of the vapor generator. The three sampling chambers were monitored alternately during sample collection. The generator conditions used are given in the following table:

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Generator Conditions
for
1,1,2,2-Tetrachloro-1,2-difluoroethane

Nitrogen flow rate	0.208 liter/minute at 25°C
Dilution air flow rate	31.6 liters/minute at 25°C
Bath temperature	35°C

A gas chromatograph was used to monitor the generated vapor concentrations (Reference No. 1). Samples were collected for 43.5 minutes at a rate of approximately 0.050 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for 2-Butanone (Reference No. 3). Less than 5% of the generated concentration of 6990 mg/cu m was present in the effluent after 3 hours. Sampling was done at a rate of 0.041 liter per minute, indicating a capacity of at least 52 mg of the analyte in the charcoal tube.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for 1,1,2,2-tetrachloro-1,2-difluoroethane as in Reference No. 4.

The sampling and analysis data gave a chi squared value of 11.0, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for 1,1,2,2-tetrachloro-1,2-difluoroethane show excellent precision. Therefore, pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on all the data.

The statistical procedures used are described in Reference No. 5.

$$\overline{CV}_1 = 0.005 \qquad \overline{CV}_2 = 0.021 \qquad \overline{CV}_T = 0.054$$

The average recovery at the OSHA standard level was 102.6%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: 1,1,2,2-Tetrachloro-1,2-difluoroethane, S132

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
4.13	3.94	0.954	8.37	8.17	0.976	17.22	16.86	0.979
4.13	3.93	0.952	8.37	8.17	0.976	17.22	16.88	0.980
4.13	3.96	0.959	8.37	8.14	0.973	17.22	16.97	0.985
4.13	3.92	0.949	8.37	8.06	0.963	17.22	17.09	0.992
4.13	3.94	0.954	8.37	8.09	0.967	17.22	16.96	0.985
4.13	3.93	0.952	8.37	8.08	0.965	17.22	17.04	0.990
n =		6			6			6
mean		0.953			0.970			0.985
std dev		0.003			0.006			0.005
CV_1		0.003			0.006			0.005

$\overline{CV}_1$ 0.005

$\overline{CV}_{A+\overline{DE}}$ 0.005

The equation D.E. = $0.978 - e^{-0.937 \times \text{mg found}}$ was used to to calculate the corr mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 6.

Data Sheet: 1,1,2,2-Tetrachloro-1,2-difluoroethane, S132

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	3.74	3.95	2.013	1962	1883	
	3.90	4.10	2.052	1998	1883	
	3.84	4.04	2.060	1961	1883	
	3.70	3.91	2.008	1947	1883	
	3.94	4.13	2.069	1996	1883	
	3.82	4.02	2.004	2006	1883	
			n = 6			
			mean	1978		105.0%
			std dev	25		
			CV_2	0.013		
1S	7.90	8.09	2.017	4010	3880	
	7.76	7.94	1.987	4000	3880	
	7.80	7.98	2.021	3950	3880	
	7.80	7.98	2.013	3960	3880	
	7.85	8.03	2.017	3980	3880	
	(Sample was lost.)					
			n = 5			
			mean	3980		102.6%
			std dev	25		
			CV_2	0.006		
2S	15.61	15.96	2.000	7980	8060	
	15.60	15.95	2.039	7820	8060	
	15.57	15.92	1.991	8000	8060	
	10.22	10.45	1.335	7830	8060	
	9.88	10.10	1.213	8330	8060	
	14.69	15.02	1.978	7590	8060	
			n = 6			
			mean	7930		98.4%
			std dev	250		
$\overline{CV}_2$	0.021		CV_2	0.032		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 7.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, 2-Butanone, No. S3, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

5. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

6. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W.J. Dixon, ed., p. 387,(University of California Press, Los Angeles, California, 1973).

7. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Chlorobenzene, No. S133

OSHA Standard: 75 ppm (345 mg/cu m)

Chemical used for validation: Chlorobenzene
J. T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of chlorobenzene in air is described in NIOSH Method S133, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid chlorobenzene to represent 10-liter air samples. Samples of chlorobenzene in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of chlorobenzene in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 54.7 minutes). The "true" concentrations of chlorobenzene in the generated samples were determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There were no major modifications of P&CAM 127.

Generation

Samples of chlorobenzene in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions
for
Chlorobenzene

Nitrogen flow rate	0.39 liter/minute at 25°C
Dilution air flow rate	40.5 liters/minute at 25°C
Bath temperature	30°C

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 1). The three sampling chambers were monitored alternately during sample collection. Samples were collected for 54.7 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 1). Less than 5% of the generated concentration of 704 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.185 liter per minute, indicating a capacity of at least 31 mg of chlorobenzene in the charcoal tube.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.025$ $\overline{CV}_2 = 0.022$ $\overline{CV}_T = 0.056$

The average recovery at the OSHA standard level was 103.3%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Chlorobenzene, S133

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.770	1.666	0.941	3.54	3.17	0.895	7.08	6.49	0.917
1.770	1.537	0.868	3.54	3.21	0.907	7.08	6.53	0.922
1.770	1.568	0.886	3.54	3.16	0.893	7.08	6.63	0.936
1.770	1.617	0.914	3.54	3.17	0.895	7.08	6.43	0.908
1.770	1.608	0.908	3.54	3.33	0.941	7.08	6.25	0.883
1.770	1.546	0.873	3.54	3.32	0.938	7.08	6.40	0.904
n =		6			6			6
mean		0.898			0.912			0.912
std dev		0.028			0.022			0.018
CV_1		0.031			0.024			0.020

$\overline{CV}_1$ 0.025

$\overline{CV}_{A+\overline{DE}}$ 0.027

The equation D.E. = $0.913 - e^{-2.749 \times \text{mg found}}$ was used to calculate the corr mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 4.

Data Sheet: Chlorobenzene, S133

Sampling and Analysis

Test Level	Found mg	Found Corr mg	Found Liters	Found mg/cu m*	Taken mg/cu m	Recovery
0.5S	1.663	1.842	10.45	176.3	183	
	1.673	1.853	10.28	180.2	183	
	1.683	1.864	10.50	177.5	183	
	1.704	1.885	10.83	174.0	183	
	1.786	1.971	11.38	173.2	183	
	1.691	1.873	10.99	170.4	183	
			n = 6			
			mean	175.3		95.8
			std dev	3.5		
			CV_2	0.020		
1S	3.03	3.32	8.97	370	365	
	3.24	3.55	9.57	371	365	
	3.21	3.52	9.08	388	365	
	3.08	3.37	9.24	365	365	
	2.92	3.20	8.42	380	365	
	3.39	3.71	9.57	388	365	
			n = 6			
			mean	377		103.3
			std dev	10		
			CV_2	0.027		
2S	6.87	7.52	10.12	743	736	
	7.13	7.81	10.28	760	736	
	6.88	7.54	10.17	741	736	
	6.81	7.46	9.96	749	736	
	6.83	7.48	10.12	739	736	
	7.12	7.80	10.12	771	736	
			n = 6			
			mean	750		101.9
			std dev	13		
$\overline{CV}_2$	0.022		CV_2	0.017		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: 1,1,2-Trichloroethane, No. S134

OSHA Standard: 55 mg/cu m

Chemical used for validation: 1,1,2-Trichloroethane (95%), Aldrich

Procedure

The general procedure used is described in NIOSH Method No. S134 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of 1,1,2-trichloroethane represented in a 10-liter air sample. To minimize errors associated with volume measurements of less than 1 microliter, a solution of 1,1,2-trichloroethane in carbon disulfide was used. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using octane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modification of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 11.15 mg/min of 1,1,2-trichloroethane via a syringe injector to a dry air stream flowing at a rate of 0.1008 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 44 minutes (10 liters). The data reported is for the third set of 18 samples collected. Initial generation of 1,1,2-trichloroethane presented some problems resulting in low recovery, 79%,with poor precision, $\overline{CV}_2 = .0.086$. This low recovery is associated with problems in calibrating the generator concentration. In the subsequent experiments, the heated injection port was used and the unit was tested for probable leaks. The generator concentration was also verified by comparing with the total hydrocarbon response of M^3 dosed with 76 microliters (110 mg) of 1,1,2-trichloroethane. The response of the total hydrocarbon analyzer for both the generator and the M^3 were identical, thus confirming the generator 2X test level concentration estimated to be 110.6 mg/cu m. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report. A description of M^3 may be found in the Propane S87 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 4.9 mg of 1,1,2-trichloroethane when a test atmosphere containing 108 mg/cu m of 1,1,2-trichloroethane in air was sampled at 0.19 liters per minute for 240 minutes; i.e. at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0099 \qquad \overline{CV}_2 = 0.0261 \quad \overline{CV}_T = 0.0565$$

The average recovery of the generated samples over all levels was

$$91 \pm 8.2\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: 1,1,2-Trichloroethane S134

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.2887	0.2807	0.972	0.577	0.559	0.969	1.155	1.114	0.965
0.2887	0.2776	0.962	0.577	0.556	0.964	1.155	1.110	0.961
0.2887	0.2784	0.964	0.577	0.562	0.974	1.155	1.118	0.968
0.2887	0.2773	0.961	0.577	0.562	0.974	1.155	1.113	0.964
0.2887	0.2785	0.965	0.577	0.563	0.976	1.155	1.100	0.952
0.2887	0.2714	0.940	0.577	0.555	0.962	1.155	1.138	0.985
n =		6			6			6
mean		0.961			0.970			0.966
std dev		0.0108			0.0058			0.0109
CV_1		0.0113			0.0060			0.0113

$\overline{CV}_1$ 0.0099

$\overline{CV}_{A+\overline{DE}}$ 0.0106

Data Sheet: 1,1,2-Trichloroethane S134

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.2257	0.2376	9.90	24.00	26.37	
	0.2235	0.2353	9.90	23.76	26.37	
	0.2199	0.2315	9.90	23.38	26.37	
	0.2177	0.2292	9.90	23.15	26.37	
	0.2263	0.2382	9.90	24.06	26.37	
	0.2388	0.2514	9.90	25.39	26.37	
			n = 6			
			mean	23.96		90.9
			std dev	0.786		
			CV_2	0.0328		
1S	0.494	0.515	9.90	52.0	54.4	
	0.466	0.485	9.81	49.4	54.4	
	0.479	0.499	9.72	51.3	54.4	
	0.492	0.513	10.07	50.9	54.4	
	0.470	0.490	9.94	49.3	54.4	
	0.457	0.476	9.85	48.3	54.4	
			n = 6			
			mean	50.2		92.3
			std dev	1.414		
			CV_2	0.0282		
2S	0.996	1.027	10.21	100.6	110.6	
	0.950	0.979	9.94	98.5	110.6	
	0.963	0.993	9.94	99.9	110.6	
	0.967	0.997	9.90	100.7	110.6	
	0.971	1.001	10.29	97.3	110.6	
	0.958	0.988	9.94	99.4	110.6	
			n = 6			
			mean	99.4		89.9
			std dev	1.312		
			CV_2	0.0132		
			$\overline{CV}_2$	0.0261		

Backup Data Report

Substance: o-Dichlorobenzene

OSHA Standard: 300 mg/cu m - Ceiling

Chemical used for validation: o-Dichlorobenzene, 99%; Fisher Chemical Co.

Procedure

The general procedure used is described in NIOSH Method No. S135 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of o-dichlorobenzene represented in a 3-liter air sample. To minimize errors associated with volume measurements of less than 1 microliter, a solution of o-dichlorobenzene in carbon disulfide was used. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 63.7 mg/min of o-dichlorobenzene via a syringe injector to a dry air stream flowing at a rate of 0.1013 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 15 minutes (3.4 liters). The data reported is for the second set of 18 samples collected. The generation and collection has been repeated because the recovery for the first set was low, 88%. This low recovery is associated with problems in calibrating the generator concentration. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 29.9 mg of o-dichlorobenzene when a test atmosphere containing 655 mg/cu m of o-dichlorobenzene in air was sampled at 0.19 liters per minute for

240 minutes; i.e. at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. The breakthrough data are based on a prior experiment.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0131 \qquad \overline{CV}_2 = 0.0450 \qquad \overline{CV}_T = 0.0675$$

The average recovery of the generated samples over all levels was

$$97.6 \pm 8.5\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: o-Dichlorobenzene

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.467	0.417	0.893	0.934	0.788	0.844	1.868	1.622	0.868
0.467	0.404	0.865	0.934	0.792	0.848	1.868	1.614	0.864
0.467	0.409	0.876	0.934	0.800	0.857	1.868	1.627	0.871
0.467	0.396	0.848	0.934	0.787	0.843	1.868	1.629	0.872
0.467	0.402	0.861	0.934	0.796	0.852	1.868	1.593	0.853
0.467	0.396	0.848	0.934	0.800	0.857	1.868	1.621	0.868
n =		6			6			6
mean		0.865			0.850			0.866
std dev		0.0173			0.0062			0.0070
CV_1		0.0200			0.0073			0.0080

$\overline{CV}_1$ 0.0131

$\overline{CV}_{A+\overline{DE}}$ 0.0142

Data Sheet: o-Dichlorobenzene

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.381	0.448	3.39	132.2	149.9	
	0.429	0.505	3.39	148.9	149.9	
	0.430	0.506	3.39	149.2	149.9	
	0.433	0.509	3.39	150.3	149.9	
	0.426	0.501	3.39	147.8	149.9	
	0.411	0.484	3.39	142.6	149.9	
			n = 6			
			mean	145.2		96.9
			std dev	6.90		
			CV_2	0.0475		
1S	0.860	1.006	3.39	296.7	309	
	0.865	1.012	3.36	301	309	
	0.862	1.008	3.33	303	309	
	0.853	0.998	3.45	289.3	309	
	0.885	1.035	3.41	304	309	
	0.871	1.019	3.38	301	309	
			n = 6			
			mean	299.2		96.8
			std dev	5.44		
			CV_2	0.0182		
2S	1.806	2.100	3.50	600	629	
	1.856	2.158	3.41	633	629	
	1.638	1.905	3.41	559	629	
	1.892	2.200	3.39	649	629	
	1.970	2.291	3.53	649	629	
	1.904	2.214	3.41	649	629	
			n = 6			
			mean	623		99.0
			std dev	36.8		
			CV_2	0.0591		
			$\overline{CV}_2$	0.0450		

Backup Data Report

Substance: Diazomethane, No. S137

OSHA Standard: 0.4 mg/cu m

Chemical used for validation: Diazald®, Aldrich Chemical Company

Procedure

No method was previously available for collection and analysis of diazomethane in air. Samples of diazomethane in air were generated by the procedure described below, and the analyte collected in glass tubes containing a solid support, XAD-2, coated with octanoic acid. Collection efficiency tests were done at 2 times the OSHA Standard. Desorption efficiency tests were done at 0.5, 1 and 2X OSHA standard by spiking with the appropriate volume of methyl octanoate, the reaction product of diazomethane and octanoic acid. The methyl octanoate added is equivalent to that present in a 10-liter sample at each of the three test levels. The resin used was XAD-2 supplied by Rohm and Haas, Philadelphia, Pa. and coated with octanoic acid. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using tridecane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in NIOSH Method No. S137. Other related descriptive details of the instrumentation used may be found in the Butyl Acetate S47 Backup Data Report.

Analysis

Diazomethane is unstable, even in solution and is extremely difficult to handle. For this reason, diazomethane was trapped and analyzed as the methyl ester of octanoic acid. The validation of the analytical method was done using methyl octanoate for spiking and for the preparation of the calibration curve.

The GC analysis was done on a column 10' x 1/8" SS packed with 5% SP-1000 in 100/120 mesh Supelcoport with a pre-column, 6" x 1/8" SS packed with 10% Carbowax 20 M + 1.2% NaOH on 80/100 mesh Gas Chrom Q. The precolumn traps the octanoic acid effectively and eliminates the need for the long analysis time required to elute the octanoic acid A non-polar column, 10' x 1/8" SS, 10% OV-101, without the pre-column was also studied. Good resolution of methyl octanoate from octanoic acid can be obtained at a column temperature of 125°C but the analysis time is more than 1 hour per sample. On the other hand, a polar column such as 10% FFAP and 5% SP-1000 without the pre-column retains the octanoic acid at 95°C so that it is possible to inject a few samples before the octanoic acid shows up. Ultimately, however, it is

still necessary to elute the octanoic acid build-up to avoid messy chromatograms. Thus the use of the pre-column is recommended.

Generation

Diazomethane is not an item of commerce; it must be prepared in situ from a suitable precursor immediately prior to use. A typical procedure (Reference 1) involves dropwise addition of an ethereal solution of a nitrosamide precursor to a stirred reaction pot containing strong base. Ether and diazomethane distill out of the pot, which is held at 70°C and are condensed in a cold trap. The "product" is thus an ethereal solution of diazomethane.

Yield is determined by adding an aliquot of the solution to an excess of benzoic acid in ether and titrating the excess acid.

The ethereal diazomethane solutions must be kept cold (0°C), protected from light, and handled with care, since they have been known to explode. Any sharp edges (ground glass surfaces, crystals separating from supersaturated solution, broken sticks of KOH used as drying agent) may serve to trigger an explosion. In organic synthesis work, the cold diazomethane solution is added to a cold solution of other reactant and the mixture is kept cold until reaction is complete, as indicated by complete disappearance of the yellow diazomethane color.

For purposes of the NIOSH Methods Validation program, it was necessary to be able to generate a room temperature atmosphere of diazomethane in air over periods of up to 4 hours. Because of the instability problems noted above, it was apparent that the batch preparation of diazomethane in ether and slow delivery of the solution via syringe to the vapor generation/dilution system was likely to present hazards. Thus, a procedure for the continuous generation of diazomethane at an appropriate rate was devised.

Preliminary experiments showed that the procedure of Reference 1 could be modified to suit the needs of the present program. A reaction pot was charged with 1 ml of 60% KOH and 2-4 ml of 2-(2-ethoxy ethoxy)-ethanol and heated to 70°C with magnetic stirring. A 0.1 M solution of N-methyl-N-nitroso-p-toluenesulfonamide (Diazald®) was added through a syringe needle at 0.1 ml/min. A 1-liter per minute air stream was passed over the surface of the reaction mixture in order to sweep volatile reaction products through 2 bubblers in series containing a solution of benzoic acid in xylene. At the end of the run, the bubbler contents and rinsings were transferred to 50-ml volumetric flasks and made to volume with xylene. The yield of methyl benzoate, and hence of diazomethane, was determined by titration of excess acid with aqueous NaOH. At the lowest concentration levels, the yield of diazomethane was determined by GC analysis of methyl benzoate. The yield of diazomethane varied with diazald concentration and addition rates as shown below. It seemed probable that the fluctuation of per cent yield with concentration was due to side reactions.

Diazald Concentration M	Rate of Addition mℓ/min	% Yield
0.10	0.100	36
0.10	0.059	20
0.125	0.059	35
0.18	0.059	65

In an attempt to minimize this problem, the temperature of the reaction pot was reduced from 70°C to ambient (25°C). At this temperature and an addition rate of 0.059 ml/min the yield was reproducibly 67% over a concentration of 0.04 to 0.125 M Diazald®.

In order to generate an atmosphere of diazomethane in air at 2X the OSHA standard, the vapor generation/dilution system described in the S47 Butyl Acetate Backup Data Report was modified as shown schematically in Figure 1.

Diazald® (Aldrich Chemical Company, Inc.) was dissolved in anhydrous diethyl ether to make a 0.0467 M solution. [NOTE: Some decomposition accompanies dissolution as evidenced by a crackling sound.] This solution was added, via a blunt ended Teflon needle, syringe, and syringe drive, below the surface of a mixture of 6 ml of 2-(2-ethoxy ethoxy)-ethanol and 1.5 ml 60% aqueous KOH in a 50-ml round-bottomed flask. [NOTE: The mixture must be shaken or stirred vigorously before addition begins to ensure a homogeneneous system.] The addition rate was 0.059 ml/min. A portion of the Main Line air flow was used to sweep the gaseous reaction products into the dilution line. No net change in the calibration air flow occurred because the same amount of air was removed and returned. The generation reaction was run at room temperature.

The concentration of diazomethane generated was determined by passing the effluent air stream from the reaction vessel through a solution of benzoic acid in xylene using fritted glass bubblers. The methyl benzoate formed was analyzed by gas chromatography. Collection efficiency of the bubblers, determined by running two bubblers in series, was 100%. The yield of diazomethane, based on Diazald, was 65-69%. Yields reported in Reference 1 using high concentrations of Diazald vary from 64 to 73%.

Diazomethane was delivered at a rate of 0.078 mg/min to the dry air stream flowing at a rate of 0.1008 cu m/min at 26°C and 765 mm Hg. The dilution ratios of the three sample lines were maintained at 0.230, 0.485, and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 44 min (10 liters).

Collection Efficiency

The collection efficiency of the coated resin tubes was determined over a period of 4 hours, at time intervals ranging from 45-240

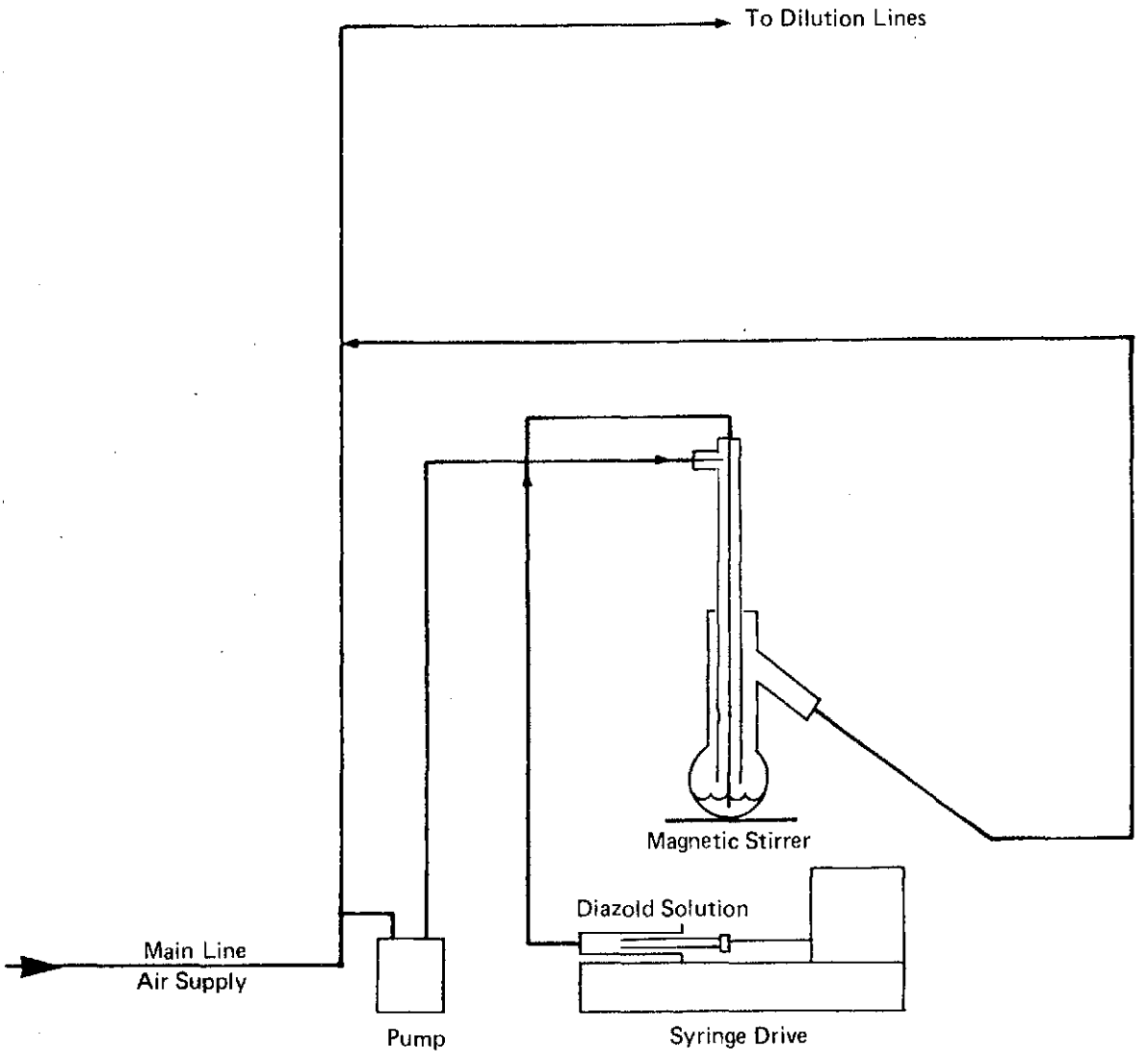


FIGURE 1 DIAZOMETHANE GENERATOR

minutes at 0.22 liters per minute (10-54 liters). Tests were done for an air sample concentration of 0.751 and 0.829 mg/cu m. Each tube was analyzed separately and the relative amount of diazomethane collected in the primary and backup tubes was determined, based on the total µg found in both tubes. From the 12 samples collected, the average collection efficiency in the first tube is 99.7 $\pm$ 0.8%. (See Table 1.)

The first section of the XAD-2 tube was found to hold at least 0.045 mg of diazomethane when a test atmosphere containing 0.829 mg/cu m of diazomethane in air was sampled at 0.22 liters per minute for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 2.

$\overline{CV}_1 = 0.0242$ $\overline{CV}_2 = 0.0669$ $\overline{CV}_T = 0.0841$

$\overline{CV}_2$ and $\overline{CV}_T$ were calculated from data from 35 samples across 3 concentration levels.

The average recovery of the generated samples was found to vary in a reproducible manner with the diazomethane concentration as shown below.

Level	% Recovery
0.5S	70.2
1S	90.2
2S	90.2

The low recovery at the 0.5S level appears to be real and is not attributable to an uncertainty in the actual concentration of diazomethane at that level. Thus, this recovery value must be used as a correction factor in order to determine the "true" diazomethane concentrations, particularly at low diazomethane concentrations. It is conceivable that the low recovery in fact arises from a relatively low "cross section" for reaction of diazomethane with octanoic acid at low concentrations. If this is true it might be possible to increase the recovery at the 0.5S level by increasing the octanoic acid loading from 1% to 2% by weight of resin. Alternatively, one could simply include a recovery factor in calculating the air sample diazomethane concentration, as is recommended in the Sampling and Analysis Method.

References

1. T. J. de Boer and H. J. Backer, Org. Syn., Coll. Vol. 4, John Wiley and Sons, New York, N.Y., 1963, p. 250.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Collection Efficiency Data

Sample Size (In liters)	µg Diazomethane Collected in Tube[a]				
	Front	Backup	Total	% in Front	Generator Concentration mg/cu m
10.15	6.67	0.000	6.670	100.0	0.751
10.24	7.77	0.002	7.772	100.0	0.751
10.68	7.34	0.000	7.340	100.0	0.751
10.24	6.96	0.013	6.973	99.8	0.751
10.24	7.64	0.000	7.640	100.0	0.751
10.20	6.74	0.023	6.763	99.7	0.751
26.65	19.78	0.04	19.82	99.8	0.829
26.89	20.39	0.59	20.98	97.1	0.829
42.03	27.70	0.02	27.72	99.9	0.829
40.42	26.94	0.02	26.96	99.9	0.829
53.96	39.40	0.02	39.42	99.9	0.829
53.7	39.62	0.05	39.67	99.9	0.829

Overall Average Collection Efficiency
$99.7 \pm 0.8\%$

[a]These values have been corrected for desorption efficiency, and converted from µg of methyl octanoate to µg of diazomethane by multiplying by 42.01/158.2.

Data Sheet: Diazomethane, S137

Analysis

Level	0.5S			1S			2S	
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
7.90	8.02	1.015	15.80	16.35	1.035	31.6	31.9	1.009
7.90	8.21	1.039	15.80	17.01	1.077	31.6	32.1	1.016
7.90	8.52	1.078	15.80	16.70	1.057	31.6	32.0	1.013
7.90	8.06	1.020	15.80	16.06	1.016	31.6	31.8	1.006
7.90	8.42	1.066	15.80	15.68	0.992	31.6	32.1	1.016
7.90	8.62	1.091	15.80	16.36	1.035	31.6	32.3	1.022
n =		6			6			6
mean		1.052			1.035			1.014
std dev		0.0315			0.0293			0.0057
CV_1		0.0299			0.0288			0.0056

$\overline{CV}_1$ 0.0242

$\overline{CV}_{A+\overline{DE}}$ 0.0261

[a]All values reported as µg. Methyl octanoate used for spiking in amounts equivalent to the corresponding levels of diazomethane required (1 mole methyl octanoate = 1 mole diazomethane). All values corrected for blank of 0.31 µg.

Data Sheet: Diazomethane, S137

Sampling and Analysis I

Test Level	Found				Taken	
	µg	Corr µg[a]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.75	1.221	10.53	0.1160	0.1727	
	5.02	1.290	10.24	0.1260	0.1727	
	4.67	1.200	10.20	0.1176	0.1727	
	5.58	1.434	10.42	0.1376	0.1727	
	2.97	0.763*	10.02	0.0761*	0.1727	
	5.01	1.288	10.15	0.1269	0.1727	
			n = 5			
			mean	0.1248		72.3
			std dev	0.0086		
			CV_2	0.0689		
1S	12.89	3.31	10.24	0.323	0.364	
	13.18	3.39	10.20	0.332	0.364	
	13.04	3.35	10.42	0.321	0.364	
	12.18	3.13	10.24	0.306	0.364	
	13.16	3.38	10.24	0.330	0.364	
	13.08	3.36	10.24	0.328	0.364	
			n = 6			
			mean	0.323		88.7
			std dev	0.010		
			CV_2	0.0310		
2S	25.96	6.67	10.15	0.657	0.751	
	30.24	7.77	10.24	0.759	0.751	
	28.57	7.34	10.68	0.687	0.751	
	27.07	6.96	10.24	0.680	0.751	
	29.72	7.64	10.24	0.746	0.751	
	26.23	6.74	10.20	0.661	0.751	
			n = 6			
			mean	0.698		92.9
			std dev	0.044		
			CV_2	0.0630		
			$\overline{CV}_2$	0.0558		

[a]Corrected for DE and molecular weight ratio, 42.04/158.24
*These values excluded from statistical analysis.

Data Sheet: Diazomethane, S137

Sampling and Analysis II

Test Level	Found				Taken	
	µg	Corr µg[a]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.67	1.201	9.85	0.1219	0.1835	
	5.14	1.321	9.94	0.1329	0.1835	
	5.15	1.324	9.90	0.1337	0.1835	
	4.38	1.126	10.11	0.1114	0.1835	
	4.48	1.152	9.72	0.1185	0.1835	
	5.07	1.303	9.85	0.1323	0.1835	
			n = 6			
			mean	0.1251		68.2
			std dev	0.00925		
			CV_2	0.0739		
1S	14.39	3.70	9.94	0.372	0.387	
	13.78	3.54	9.90	0.358	0.387	
	14.54	3.73	10.11	0.369	0.387	
	11.83	3.04	9.94	0.306	0.387	
	14.83	3.70	9.94	0.372	0.387	
	13.71	3.52	9.94	0.354	0.387	
			n = 6			
			mean	0.355		91.7
			std dev	0.0252		
			CV_2	0.0710		
2S	30.77	7.91	9.85	0.803	0.798	
	28.62	7.36	9.94	0.740	0.798	
	28.92	7.43	10.33	0.719	0.798	
	23.84	6.13	9.94	0.617	0.798	
	24.87	6.39	9.94	0.643	0.798	
	25.66	6.60	9.90	0.667	0.798	
			n = 6			
			mean	0.698		87.5
			std dev	0.0690		
			CV_2	0.0988		
			$\overline{CV_2}$	0.0822		

[a]Corrected for DE and molecular weight ratio, 42.04/158.24

Backup Data Report

Substance: Diethylamine, No. S139

OSHA Standard: 75 mg/cu m

Chemical used for validation: Diethylamine, Fisher Chemicals, reagent grade

Procedure

The general procedure used is described in NIOSH Method No. S139 which has been adapted from P&CAM 168. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of diethylamine represented in a 10-liter air sample. The silica gel used was the 20/40 mesh type supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using n-propanol as internal standard.

The analyte was desorbed from the silica gel with 0.2 N sulfuric acid in 10% methanol. The desorption process was carried out for three hours in an ultrasonic bath to obtain adequate desorption. The sample vials were tightly capped to minimize evaporation losses during the desorption process. At the end of the desorption period, the samples were removed from the ultrasonic bath and allowed to stand for a few minutes to allow the silica gel particles to settle. A 500-microliter aliquot of the clear, supernatant liquid was carefully drawn and transferred to another vial. This acidic extract was treated with 500 microliters of 0.3 N potassium hydroxide to release the free amine and a 1.0 microliter aliquot of the resulting basic solution was analyzed. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Other related descriptive details of the instrumentation used may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 168 was modified with respect to the silica gel sampling tube size, the solvent used for desorption and also the desorption period required. The necessity for these modifications is addressed in the experimental discussion below.

Experimental Discussion

Initial experiments on the aliphatic amines, including n-butylamine, diisopropylamine and diethylamine were set up to determine the more suitable absorbent media for these primary and secondary amines. Desorption efficiency experiments were set up to compare charcoal

and silica gel. Duplicate samples were spiked on 150 mg of silica gel and 100 mg of Lot 105 charcoal and the samples were desorbed with 0.1 N sulfuric acid for 30-120 minutes. (No rigorous control of desorption period was employed.) Aliquots of the corresponding sample extracts were treated with an equal volume of 0.2 N potassium hydroxide solution and 1.0-microliter aliquots of these basic solutions were analyzed. The data summarized below indicates that silica gel is preferable to charcoal because the desorption efficiency using the 0.1 N H_2SO_4 was higher.

Comparison of Desorption Efficiency for Silica Gel and Charcoal

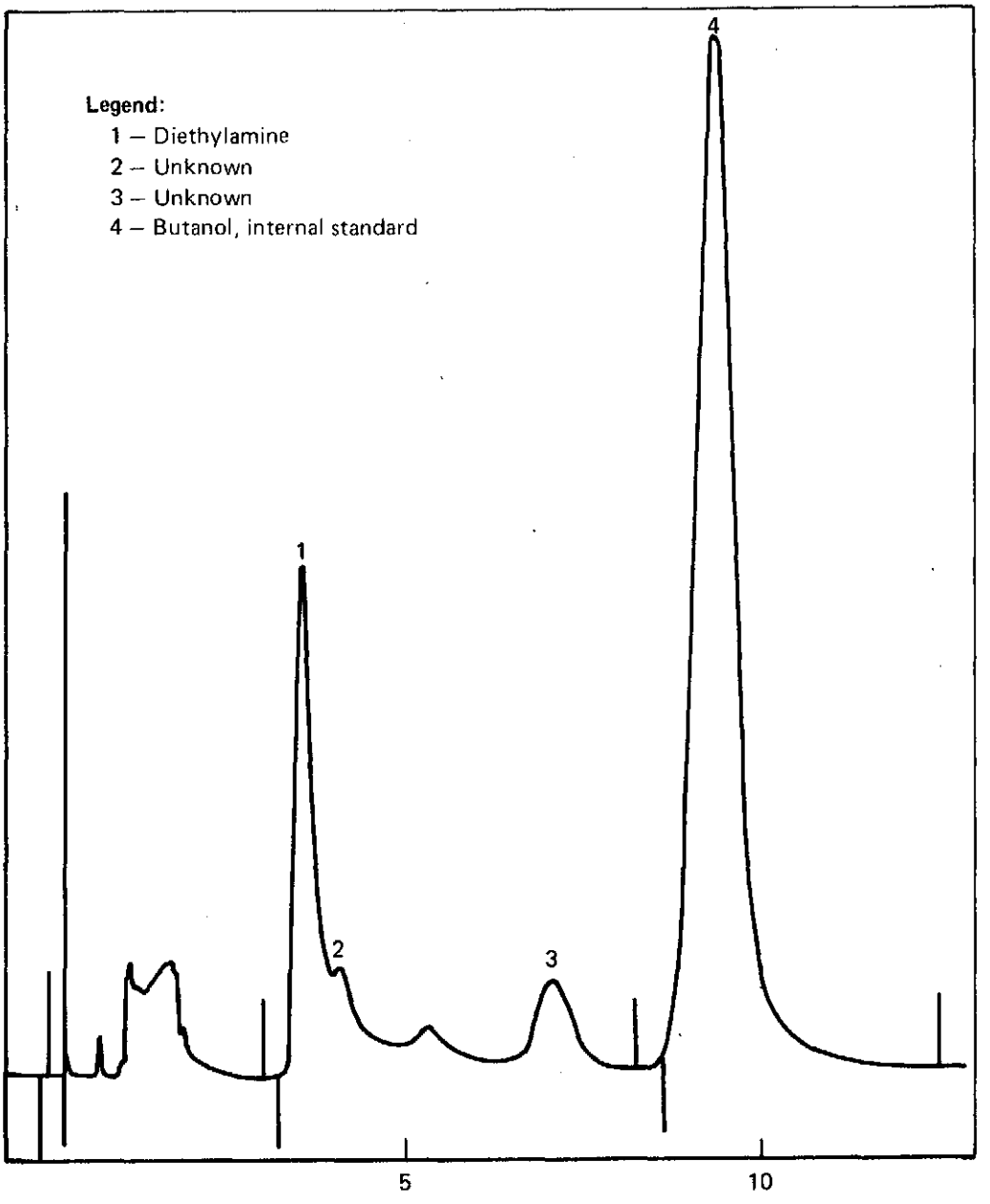
Compound	Amount Added	Average DE	
		Silica Gel	Charcoal
Diethylamine	0.78 mg	0.73	0.35
n-Butylamine	0.45 mg	0.69	0.01
Diisopropylamine	0.45 mg	0.46	0.07

Similar initial screening experiments were also set up to determine whether pure organic solvents such as methanol, ethanol, carbon disulfide and chloroform would be useful solvents. Direct injection of 1.0-microliter aliquots of these solvents into the gas chromatographic column chosen (6' x 1/4" glass column, 2 mm ID, packed with 4% Carbowax 20 M + 0.8% KOH on Carbosieve B) showed very broad tailing solvent peaks plus impurities which completely hid the component peaks. Thus, all subsequent studies were confined to aqueous systems.

Early experiments also revealed that the acidic extracts should not be basicified in the presence of silica gel. A silica gel sample spiked with 0.74 mg of diethylamine was desorbed with 1.0 ml of 0.1 N H_2SO_4 for 60 minutes and then treated with 0.8 ml of 0.2 N potassium hydroxide in the presence of the silica gel. The basic solution was then analyzed at periodic time intervals. A progressively decreasing amount of diethylamine was found, probably due to readsorption and decomposition losses. A chromatogram of the sample five minutes after base treatment is shown in Figure 1, and the reaction time data are summarized in Table 1.

Acid aqueous solutions such as 0.1 N H_2SO_4 and 0.2 N H_2SO_4; and 0.1 N HCl and 0.2 N HCl were tried for desorption efficiency tests (60 minutes) in conjunction with continuous ultrasonic agitation. The results of a limited number of tests indicated that 0.2 N H_2SO_4 gave the highest desorption efficiency with the best precision, 79.7 $\pm$ 0.5%. Time studies with this solvent indicated that a three-hour desorption time in the ultrasonic agitator is adequate.

The first set of spiked samples representative of a 10-liter sample at the 0.5, 1, and 2X OSHA standard gave low DE values of 0.62, 0.74, and 0.79 respectively and poor precision, $\overline{CV}_1 = 0.0773$. Subsequently, another set of spiked samples for a 50-liter sample at the three test levels was studied. As expected, higher DE values were obtained, 0.79, 0.86 and 0.84 respectively with better precision, $\overline{CV}_1 = 0.0498$.



Column: 6' x ¼" glass column, 2 mm ID, packed with 4% Carbowax 20 M + 0.8% KOH on Carbosieve B

FIGURE 1 CHROMATOGRAM OF DIETHYLAMINE: ACIDIC EXTRACT BASICIFIED IN THE PRESENCE OF SILICA GEL

Table 1

GC Assay of Diethylamine: Acidic Extract Basicified in the Presence of Silica Gel

Reaction Time in minutes	% Diethylamine Found Peak 1	Ratio of Peak Area to Internal Standard Peak 2	Peak 3
5	68	0.001	0.069
50	60	0.003	0.122
75	51	0.005	0.134
135	34	0.012	0.133

Two sets (18 x 2) of generated samples representing 48 liters were collected on silica gel. One set was analyzed after an overnight storage and the second set was stored for six days. The back-up sections were removed from the tubes immediately after sample collection to eliminate effects of suspected migration during storage. Analysis of the back-up sections at the 2X standard level revealed no breakthrough for the 48 liter sample. The results of these studies as summarized below indicate lower sample recovery of the stored samples.

Sample Storage (Room Temperature)	Average Recovery: Corrected for DE			
	0.5S	1S	2S	$\overline{CV}_2$
1 day	96.8	90.7	90.9	0.0263
6 days	97.0	86.0	77.7	0.0291

The above data is in agreement with a similar trend of lower DE values obtained for spiked samples stored for 10-14 days, 0.67, 0.76, 0.82, and 0.70 respectively with $\overline{CV}_1$ = 0.024. The overall trend of DE data is shown in Figure 2. Observe that the recovery for the six-day-old sample above was calculated using the DE curve for the spiked set stored for one to three days. The average recovery will increase to 90.4% if the interpolated values between the two curves shown in Figure 2 are used.

In view of the above data, attempts were made to improve the desorption efficiency of stored samples by modifying the extracting solvent with methanol. A solution of 0.2 N sulfuric acid prepared in 10% methanol was used to desorb samples spiked with 1.85, 3.55 and 7.11 mg of diethylamine. These spiked samples were stored for six days before desorption. The data summarized on page S-139-8 show an average DE of 0.817. Correspondingly, two sets of stored diethylamine collected samples were treated in the manner described above. The average recovery for the three-day-old samples is 94.9% and 95.5% for the six-day-old samples.

Generation

Test atmosphere samples at the 0.5, 1 and 2X OSHA standard test levels were generated and collected using the sample generation and collection equipment described in the Butyl Acetate S47 Backup Data Report. All six samples at the three test levels were collected simultaneously at 1.1 liters per minute for 43 minutes on the small silica gel tubes, 20/40 mesh, supplied by SKC, Inc., Pittsburgh, Pa.

Two independent methods were used to verify the generator concentration: 1) based on the syringe delivery rate and appropriate dilution air flows, and 2) based on the total hydrocarbon reading at the three dilution arms using M^3 THC data as the primary calibration. A description of M^3 may be found in the Propane S87 Backup Data Report. M^3 was dosed with a series of diethylamine aliquots ranging from 25-250 microliters (17.8 - 178 mg/cu m). The linear plot of the total hydrocarbon reading

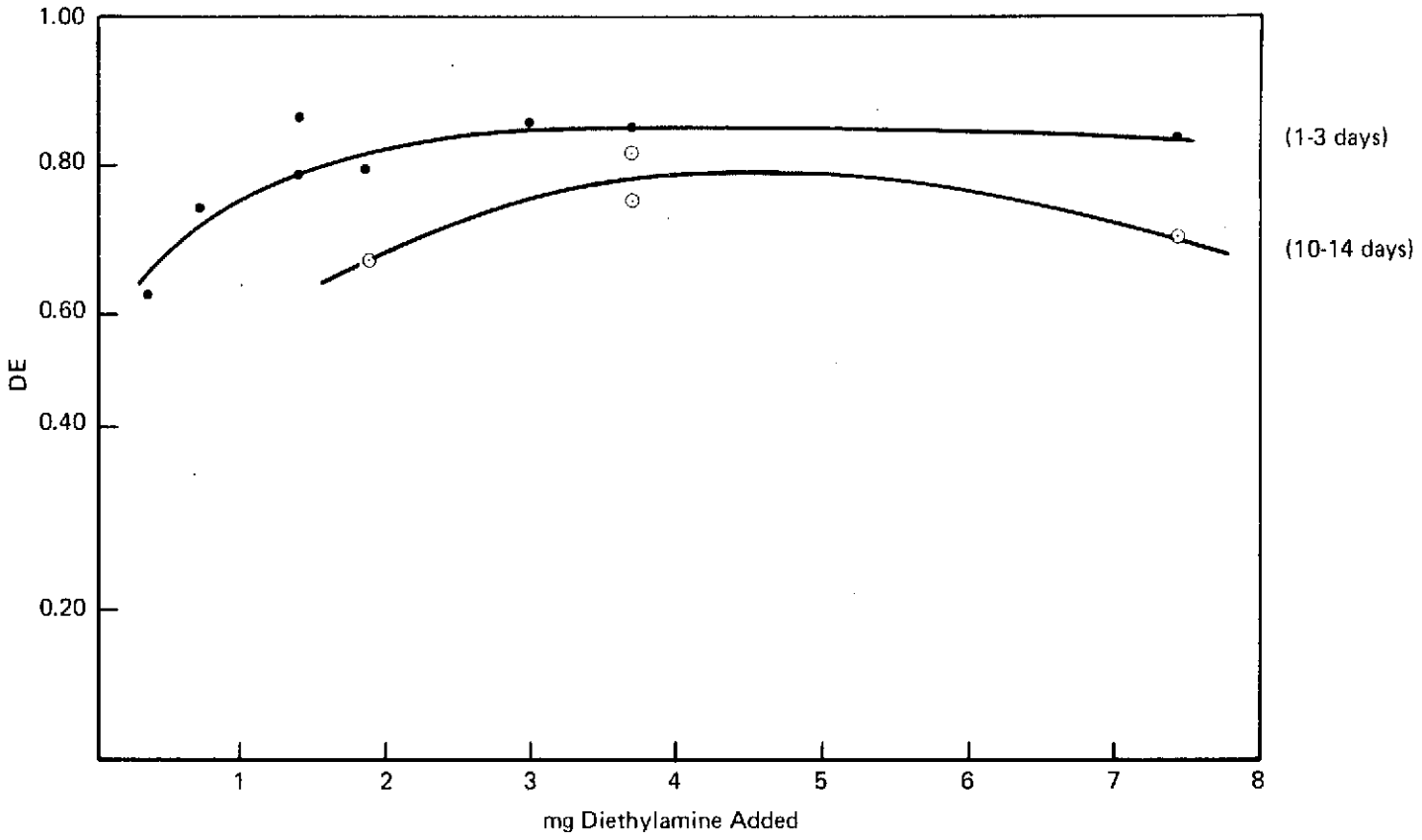


FIGURE 2 DIETHYLAMINE DE CURVE; EFFECT OF CONCENTRATION AND STORAGE TIMES
(Aqueous 0.2 N H_2SO_4, 3-hour desorption period)

against sample concentration was used to determine the generator concentration. The agreement between the two methods is excellent as shown below:

		Diethylamine Concentration in mg/cu m		
Sample Code		0.5S	1S	2S
Set 5	Syringe	35.5	73.1	148.7
(stored 3 days)	THC	35.5	74.6	159.0
Set 6	Syringe	36.0	74.5	151.3
(stored 5 days)	THC	37.6	76.0	165.1

Breakthrough

The first section of the silica gel tube was found to hold at least 7.3 mg of diethylamine when a test atmosphere containing 160.5 mg/cu m of diethylamine in air was sampled at 0.19 liters per minute for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

In addition, the backup sections of the 48-liter samples collected at 1.1 liters per minute at 2X the OSHA standard level were also analyzed. No diethylamine was found in any of the 6 backup tubes analyzed indicating that the collection efficiency is 100%.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0216 \qquad \overline{CV}_2 = 0.0486 \qquad \overline{CV}_T = 0.0703$$

The average recovery of the generated samples over all levels was

$$95.2 \pm 9.9\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

Reference

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-75.

Data Sheet: Diethylamine, S139

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.848	1.571	0.850	3.554	2.995	0.843	7.11	5.78	0.813
1.848	1.596	0.864	3.554	2.943	0.828	7.11	5.63	0.792
1.848	1.518	0.821	3.554	2.855	0.803	7.11	5.70	0.802
1.848	1.549	0.838	3.554	2.942	0.828	7.11	5.65	0.795
1.848	1.485	0.804	3.554	2.884	0.811	7.11	5.66	0.796
1.848	1.477	0.799	3.554	2.944	0.828	7.11	5.60	0.788
n =	6			6			6	
mean		0.829			0.824			0.798
std dev		0.0258			0.0143			0.0088
CV_1		0.0312			0.0173			0.0111

$\overline{CV}_1$ 0.0216

$\overline{CV}_{A+\overline{DE}}$ 0.0233

Data Sheet: Diethylamine, S139
Sampling and Analysis
(Sample stored for 3 days)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.444	1.740	47.7	36.5	35.5	
	1.423	1.714	47.1	36.4	35.5	
	1.404	1.692	47.9	35.3	35.5	
	1.142	1.376	49.0	28.1	35.5	
	1.414	1.704	48.1	35.4	35.5	
	1.362	1.641	47.1	24.8	35.5	
			n = 6			
			mean	34.4		96.9
			std dev	3.16		
			CV_2	0.0920		
1S	2.701	3.28	47.1	69.6	74.6	
	1.985*	2.40*	47.5	50.5*	74.6	
	2.879	3.50	47.5	73.7	74.6	
	2.881	3.50	47.9	73.1	74.6	
	2.871	3.49	47.5	73.5	74.6	
	2.936	3.58	47.7	75.1	74.6	
			n = 6			
			mean	73.0		97.9
			std dev	2.044		
			CV_2	0.0280		
2S	5.60	7.00	47.7	146.8	159.0	
	5.47	6.83	47.5	143.8	159.0	
	5.30	6.61	47.1	140.3	159.0	
	5.48	6.84	47,5	144.0	159.0	
	5.40	6.73	47.5	141.7	159.0	
	5.38	6.71	47.3	141.9	159.0	
			n = 6			
			mean	143.1		90.0
			std dev	2.29		
			CV_2	0.0160		
			$\overline{CV}_2$	0.0578		

*These values excluded from statistical analysis

Data Sheet: Diethylamine, S139
Sampling and Analysis
(Sample stored for 6 days)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.230	1.482	47.9	30.9	37.6	
	1.470	1.770	47.3	37.4	37.6	
	1.530	1.843	48.1	38.3	37.6	
	1.530	1.843	49.2	37.5	37.6	
	1.406	1.694	48.3	35.1	37.6	
	1.423	1.714	47.3	36.2	37.6	
			n = 6			
			mean	35.9		95.5
			std dev	2.694		
			CV_2	0.0751		
1S	2.977	3.630	47.3	76.7	76.0	
	2.071*	2.510*	47.7	52.6*	76.0	
	2.933	3.577	47.7	75.0	76.0	
	2.915	3.555	48.1	73.9	76.0	
	2.982	3.637	47.7	76.2	76.0	
	3.008	3.668	47.9	76.6	76.0	
			n = 5			
			mean	75.7		99.6
			std dev	1.203		
			CV_2	0.0159		
2S	5.93	7.46	47.9	155.7	165.1	
	5.66	7.08	47.7	148.4	165.1	
	5.91	7.43	47.3	157.1	165.1	
	5.72	7.15	47.7	149.9	165.1	
	5.68	7.10	47.7	148.8	165.1	
	5.58	6.98	47.5	146.9	165.1	
			n = 6			
			mean	151.1		91.5
			std dev	4.21		
			CV_2	0.0279		
			$\overline{CV}_2$	0.0486		

*These values excluded from statistical analysis.

Backup Data Report

Substance: Dimethylamine, No. S142

OSHA Standard: 18 mg/cu m

Chemical used for validation: Dimethylamine (99%); Welder's Supply

Procedure

The general procedure used is described in NIOSH Method No. S142 which has been adapted from P&CAM 168. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of dimethylamine represented in a 50-liter air sample. Spiking with gas samples was done by slowly adding 225, 460 and 920-microliters of dimethylamine at 29°C and 758 mm Hg to silica gel tubes containing only the front 150 mg section of 20/40 mesh silica gel from SKC, Inc., Pittsburgh, Pa. A piece of litmus paper was held at the exit end of the tube to check that no amine vapor was lost during the spiking process.

The samples were desorbed from the silica gel into 0.2 N sulfuric acid in 10% methanol. The details and rationale of the desorption procedure adapted may be found in the Diethylamine, S139 Backup Data Report. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Other related descriptive details of the instrumentation used may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 168 was modified with respect to the silica gel sampling tube size, the solvent used for desorption and also the desorption period required. The necessity for these modifications are discussed in the Diethylamine, S139 Backup Data Report. Likewise, the two separate front and backup tubes are recommended to avoid the suspected probability of migration on storage. Note, however, that migration effects were not actually tested in these studies.

Generation

Test atmosphere samples at the 0.5, 1 and 2X OSHA standard test levels were generated and collected using the sample generation and collection equipment described in the Butyl Acetate S47 Backup Data Report. All six samples at the three test levels were collected simultaneously at 1.1 liter per minute for 43 minutes on the small silica gel tubes, 20/40 mesh.

The generator concentration was determined by using the total hydrocarbon calibration curve derived from dosing M^3 with known volumes of dimethylamine gas so as to cover the entire concentration range of interest. A description of M^3 may be found in the Propane S87 Backup Data Report.

S87 Backup Data Report.

In order to test sample stability on storage, a set of freshly collected samples and a set of sample stored for 6 days at room temperature were analyzed. The data as shown on pages S142-4 and S142-5 reflect no basic difference between the 2 sets beyond normally observed experimental variations.

Breakthrough

The first section of the silica gel tube was found to hold at least 1.9 mg of dimethylamine when a test atmosphere containing 42.5 mg/cu m of dimethylamine in air was sampled at 0.19 liters per minute for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

In addition, the backup sections of the 48-liter samples collected at 1.1 liters per minute at 2X the OSHA standard level were also analyzed. No trace of dimethylamine was found in any of the 6 backup tubes analyzed indicating that the collection efficiency is 100%.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0285 \qquad \overline{CV}_2 = 0.0339 \qquad \overline{CV}_T = 0.062$$

The average recovery of the generated samples over all levels was

$$97.8 \pm 9.4\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-75.

Data Sheet: Dimethylamine, S142
Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.408	0.352	0.863	0.835	0.750	0.898	1.670	1.488	0.891
0.408	0.362	0.887	0.835	0.801	0.959	1.670	1.539	0.922
0.408	0.387	0.949	0.835	0.754	0.903	1.670	1.540	0.922
0.408	0.367	0.900	0.835	0.805	0.964	1.670	1.516	0.908
0.408	0.375	0.919	0.835	0.383*	0.459*	1.670	1.523	0.912
0.408	0.367	0.900	0.835	0.792	0.949	1.670	1.558	0.933
n =		6			5			6
mean		0.903			0.935			0.915
std dev		0.0291			0.0316			0.0145
CV_1		0.0323			0.0338			0.0159

$\overline{CV}_1$ 0.0285

$\overline{CV}_{A+\overline{DE}}$ 0.0308

* These values excluded from statistical analysis

Data Sheet: Dimethylamine, S142
Sampling and Analysis
(Sample stored for 0 days)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.321	0.361	47.7	7.57	7.26	
	0.313	0.352	47.1	7.47	7.26	
	0.325	0.363	48.0	7.56	7.26	
	0.310	0.348	49.0	7.10	7.26	
	0.328	0.367	48.2	7.61	7.26	
	0.333	0.372	47.1	7.90	7.27	
			n = 6			
			mean	7.54		103.8
			std dev	0.259		
			CV_2	0.0343		
1S	0.628	0.678	47.1	14.40	15.0	
	0.379*	0.419*	47.5	8.82*	15.0	
	0.640	0.690	47.5	14.53	15.0	
	0.621	0.671	48.0	13.98	15.0	
	0.645	0.695	47.5	14.63	15.0	
	0.642	0.692	47.7	14.51	15.0	
			n = 5			
			mean	14.41		96.1
			std dev	0.254		
			CV_2	0,0176		
2S	1.355	1.465	47.7	30.70	30.5	
	1.311	1.417	47.5	29.80	30.5	
	1.247	1.344	47.1	28.54	30.5	
	1.375	1.491	47.5	31.40	30.5	
	1.322	1.429	47.5	30.10	30.5	
	1.196	1.286	47.3	27.19	30.5	
			n = 6			
			mean	29.6		97.0
			std dev	1.525		
			CV_2	0.0515		
			$\overline{CV}_2$	0.0382		

* These values excluded from statistical analysis

Data Sheet: Dimethylamine, S142
Sampling and Analysis
(Sample stored for 6 days)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.316	0.355	47.8	7.43	7.02	
	0.300	0.337	47.2	7.14	7.02	
	0.335	0.374	48.0	7.79	7.02	
	0.314*	0.353*	49.1	7.19	7.02	
	--*	--*	48.2		7.02	
	0.334	0.373	47.2	7.90	7.02	
			n = 5			
			mean	7.49		107.7
			std dev	0.344		
			CV_2	0.0460		
1S	0.592	0.640	47.2	13.56	14.5	
	0.405*	0.448*	47.6	9.41*	14.5	
	0.705	0.758	47.6	15.92	14.5	
	0.706	0.759	48.0	15.81	14.5	
	0.703	0.756	47.6	15.88	14.5	
	0.730	0.785	47.8	16.42	14.5	
			n = 5			
			mean	15.52		110.4
			std dev	1.121		
			CV_2	0.0722		
2S	1.394	1.515	47.8	31.7	29.5	
	1.193*	1.283*	47.6	26.95*	29.5	
	1.419	1.542	47.2	32.7	29.5	
	1.426	1.550	47.6	32.6	29.5	
	1.411	1.534	47.6	32.2	29.5	
	1.401	1.523	47.4	32.1	29.5	
			n = 5			
			mean	32.3		109.5
			std dev	0.404		
			CV_2	0.0125		
			$\overline{CV}_2$	0.0500		

* These values excluded from statistical analysis

Backup Data Report

Substance:	1,1-Dimethylhydrazine, No. S143
OSHA Standard:	0.5 ppm (1 mg/cu m) - skin
Chemical Used for Validation:	1,1-Dimethylhydrazine Eastern Chemical Co.

Procedure

The procedure validated for collecting and analyzing 1,1-dimethylhydrazine in air is described in NIOSH Method S143. The analysis is based on the colorimetric molybdenum blue method described in Reference No. 1. Standard samples were prepared and a standard curve was constructed by plotting absorbance versus mg of 1,1-dimethylhydrazine. Samples of 1,1-dimethylhydrazine were generated as described below and collected in midget bubblers (impingers fitted with fritted glass tipped inlet tubes) containing 10 ml of 0.1 M hydrochloric acid. Collection efficiency tests were done at 2.22 mg/cu m. The amounts of 1,1-dimethylhydrazine found (mg) in the generated samples were determined from a standard curve. The concentrations of 1,1-dimethylhydrazine in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 101 minutes).

Modification of Reference No. 1

The intensity of the developed color was determined at 730 nm using a Cary Model 14 M spectrophotometer with a tungsten lamp.

Analysis

1,1-dimethylhydrazine standards were prepared in dilute hydrochloric acid, because standards prepared in water are unstable and must be prepared fresh daily. A time study indicated that the collected samples in dilute hydrochloric acid could be stored at room temperature as long as five days in a stoppered container before analysis with no loss. Six samples at the 1X OSHA level were prepared by spiking an appropriate amount of standard solution of 1,1-dimethylhydrazine in 0.1 M hydrochloric acid (5.0 mg/ml) into 10 ml of 0.1 M hydrochloric acid. The five day results are given on the next page.

TIME STUDY OF 1,1-DIMETHYLHYDRAZINE AFTER FIVE DAYS

µg added	µg found after 5 days		Recovery
100.0	96.5		0.965
100.0	114.0		1.140
100.0	95.5		0.955
100.0	103.5		1.035
100.0	97.5		0.975
100.0	100.5		1.005
		mean	1.013
		std dev	0.069

The results for immediate analysis are given at the 1S level in the table labeled Analysis.

Generation

1,1-Dimethylhydrazine was introduced into an air stream with an automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe filled with 1,1-dimethylhydrazine in methanol (0.789 g 1,1-dimethylhydrazine was added to 7.147 g of methanol) was placed in the syringe drive mechanism. The syringe, which was attached to a 15-in long stainless steel needle, delivered the solution at a rate of 1.456 mg/min and the analyte at a rate of 154 µg/min into a heated glass tube, heated with a heating lamp. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.56 liters/minute and diluted with air at a rate of 52.2 liters/minute to obtain a concentration of approximately two times the OSHA standard. The actual concentration in the generator was considerably lower than that predicted from the above data, so it was necessary to determine the collection efficiency of the bubbler and use this information to determine the act . levels of analyte in the air sampled. Further dilutions of the 2X level with air were made to obtain two lower concentrations. The dilution system is described in Reference No. 2.

A set of six samples at each of three concentration levels were generated and analyzed. The "true" concentration at the three levels could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates. The reason for this is unknown. It may be due to instability of 1,1-dimethylhydrazine due to oxidation and decomposition upon contact with the atmosphere (Reference No. 3). Samples were collected for 101 minutes at a flow rate of approximately 0.90 liter per minute.

Collection Efficiency

The collection efficiency was determined by connecting two bubblers in series at each of six sampling ports. The collection efficiency experiments were conducted at a concentration of 2.3 mg/cu m (as determined by analysis of the front and backup bubblers). The results are given in the following table.

COLLECTION EFFICIENCY OF 1,1-DIMETHYLHYDRAZINE

First Bubbler (mg/cu m)	Backup Bubbler (mg/cu m)	Collection Efficiency
2.218	0.025	.989
2.267	0.028	.988
2.154	0.152	.934*
2.214	0.016	.993
2.202	0.016	.993
2.262	0.023	.990
		mean 0.991
* Deleted as an outlier.		std dev 0.002

The collection efficiency in a single bubbler was sufficient so it was not considered appropriate to apply a collection efficiency correction.

Discussion

Since the solution of 1,1-dimethylhydrazine used for generation was prepared in methanol, an experiment was conducted to determine the effect of methanol in the absorption of samples. The experiment was conducted at the 1X level with six samples by spiking 100 µg into 10 ml of 0.10 M hydrochloric acid in a 50-ml volumetric flask. To this solution was added 5 microliters methanol and 10 ml phosphomolybdic acid, and the volume was made up to 50 ml with 0.1 M hydrochloric acid. The solution was transferred to a large test tube and heated in a water bath at 98°C for one hour. The solution was cooled under tap water and read at 730 nm. The results are given below:

µg spiked	µg found	% Recovery
100	90.5	90.5
100	99.0	99.0
100	94.5	94.5
100	95.5	95.5
100	106.0	106.0
100	91.5	91.5
	mean	96.2

From the above results, methanol does not affect the absorbance of 1,1-dimethylhydrazine.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for 1,1-dimethylhydrazine as in Reference No. 5.

The sampling and analysis data gave a chi squared value of 10.7 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. Therefore, CV_T is calculated only on the data at the 1X level.

$$CV_T = \sqrt{CV_2^2 + (0.05)^2} = 0.062$$

where:

CV_2 = Coefficient of Variation at the 1X level for Sampling and Analysis = 0.037

0.05 = pump error.

Data Sheet: 1,1-Dimethylhydrazine S143

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
50.0	50.5	1.010	100.0	102.0	1.020	200.0	213.0	1.065
50.0	62.5	1.250	100.0	103.5	1.035	200.0	212.0	1.060
50.0	50.5	1.010	100.0	106.0	1.060	200.0	205.0	1.025
50.0	50.0	1.000	100.0	97.5	0.975	200.0	212.0	1.060
50.0	56.5	1.130	100.0	111.5	1.115	200.0	181.5	0.908
50.0	50.0	1.000	100.0	97.0	0.970	200.0	205.5	1.028
n =		6			6			6
mean		1.067			1.029			1.024
std dev		0.103			0.055			0.060
CV_1		0.097			0.053			0.059

$\overline{CV}_1$ 0.072

$\overline{CV}_{A+\overline{AMR}}$ 0.078

Data Sheet: 1,1-Dimethylhydrazine S143

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	41.0	92.2	0.445
	50.5	96.5	0.523
	49.0	94.8	0.517
	56.0	97.6	0.574
	48.0	92.7	0.518
	44.0	96.2	0.457
		n = 6	
		mean	0.506
		std dev	0.048
		CV_2	0.095
1S	103.0	89.9	1.146
	104.5	95.6	1.093
	95.0	90.3	1.052
	102.0	98.2	1.039
	94.5	89.8	1.052
	98.5	92.9	1.060
		n = 6	
		mean	1.074
		std dev	0.040
		CV_2	0.037
2S	210.5	94.9	2.218
	213.5	94.2	2.267
	199.5	92.6	2.154
	203.5	91.9	2.214
	208.5	94.7	2.202
	225.5	99.7	2.262
		n = 6	
		mean	2.220
		std dev	0.042
$\overline{CV}_2$ = 0.060		CV_2	0.019

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No.6.

References

1. L. Feinsilver, J. A. Perregrino, and C. J. Smith, Jr., "Estimation of Hydrazine and Three of Its Methyl Derivatives," Industrial Hygiene Journal, 20, February 1959, 26-31.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Thomas Dambrauskas and Herbert H. Cornish, "A Modified Spectrophotometric Method for the Determination of Hydrazine," Industrial Hygiene Journal, March-April, 1962, 151.

4. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

5. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Ethylamine, No. S144
OSHA Standard:	10 ppm (18 mg/cu m)
Chemical Used for Validation:	Ethylamine (33% in water) Matheson, Coleman, and Bell

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 221. For determination of desorption efficiency, 150-mg samples of silica gel were placed in 2-ml Hewlett Packard automatic sample injector vials and were spiked with an aqueous solution containing .135 mg/ml of ethylamine injected with a 10-microliter syringe. The amount added was 2, 4, and 8 microliters respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 30-liter air sample at the respective level. The eluting solvent was 0.1 M sulfuric acid. Silica gel tubes were supplied by SKC, Pittsburgh, Pennsylvania, Catalog No. 226-10. Gas chromatographic analyses were performed with an automatic sampler using absolute area calibration. Details of the analytical procedures are given in the Analytical Procedure section of Reference 1, except for the desorption procedure. Satisfactory desorption required ultrasonic treatment for three hours. The eluent was then decanted from the silica gel giving a yield of approximately 0.75 ml and made alkaline with 20% sodium hydroxide to pH 10-11. Basification in the presence of the silica gel produces spurious gc peaks and permits resorption of the ethylamine.

Modifications

The method is similar to that described in P&CAM 221, which was received from NIOSH after this work was completed. Consequently, there were a number of differences:

1. A different size and type of silica gel tube was used. The mesh size of the silica gel was also different.

2. 0.1 M sulfuric acid instead of 0.5 M sulfuric acid was used for desorption. The amount of acid used for desorption was also different from the amount used in P&CAM 221.

3. 0.25 M sodium hydroxide instead of 1.1 M sodium hydroxide was used.

4. Ultrasonic treatment of the samples was needed for adequate desorption.

Generation

The test atmosphere was generated by a syringe-injection technique. Simultaneous three-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 22.6 liters per minute, and the rate of ethylamine injection was 43.1 mg/hour. Sampling time was 150 minutes with a nominal flow rate of 200 ml/min for each silica gel tube.

Breakthrough

In order to test the capacity of the silica gel tubes, an experiment was conducted at 2X the OSHA standard level (actual concentration was 31.8 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5% of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes were used to sample the test air, which was pumped through the eight tubes simultaneously through individual critical orifices. The concentration was too low to monitor, so the breakthrough experiment was run for four hours, and the backup section of the silica gel tubes analyzed for ethylamine. Breakthrough did not occur, i.e., no ethylamine was found in the backup section. Thus, the capacity of the silica gel exceeds 1.5 mg of ethylamine and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Discussion

After desorbing the analyte from the silica gel, the 0.1 M sulfuric acid solution was decanted into a small glass ampule to separate the liquid phase from the bulk of the silica gel. Approximately 0.75 ml of aqueous solution was recovered. To this solution, 50 microliters of 20% by weight solution of sodium hydroxide in water was added to give a solution with a pH of 10-11. It should be noted that the uncertainty in the final concentration resulting from the addition of 50 microliters of base to approximately 0.75 ml of solution is probably no more than 2% and was therefore, ignored in the treatment of data in this report since a similar addition of base was made to 1.0 ml-aliquots of standard solutions used for calibration tests. It is important, however, that the same technique was used for standards and collected samples to avoid a serious bias in the results. Because of this ambiguity in the validation procedure it was decided that a 0.5-ml aliquot of the acid solution above the silica gel should be pipetted into a vial for the GC analysis and 0.5 ml of 0.25 M aqueous sodium hydroxide should be added to make the solution up to exactly 1 ml with a pH greater than 11. This modification is provided in the sampling and analytical method.

The concentration of ethylamine in the aqueous solution received from Matheson, Coleman, and Bell was titrated for weak base content to a bromcresol green endpoint with 0.1 M hydrochloric acid and found to contain 32.6% ethylamine.

Precision and Accuracy

The statistical procedures are described in Reference 3.

$\overline{CV}_1 = 0.074$ $\overline{CV}_2 = 0.097$ $\overline{CV}_T = 0.113$

The average recovery of the generated samples at the 1X OSHA standard level was 102%.

Data Sheet: Ethylamine S144

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.267	0.221	0.828	0.534	0.415	0.777	1.067	0.921	0.863
0.267	0.223	0.835	0.534	0.432	0.809	1.067	0.909	0.852
0.267	0.270	1.011	0.534	0.516	0.966	1.067	1.005	0.942
0.267	0.222	0.831	0.534	0.480	0.899	1.067	1.039	0.974
0.267	0.218	0.816	0.534	0.444	0.831	1.067	0.962	0.902
0.267	0.235	0.880	0.534	0.439	0.822	1.067	0.934	0.875
n =		6			6			6
mean		0.867			0.851			0.901
std dev		0.074			0.069			0.048
CV_1		0.085			0.081			0.053

$\overline{CV}_1$ 0.074

$\overline{CV}_{A+\overline{DE}}$ 0.080

An average D.E. of 0.873 was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Ethylamine S144

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.2090	0.2394	32.6	7.34	7.41	
	0.1952	0.2236	29.1	7.68	7.41	
	0.1981	0.2269	28.2	8.05	7.41	
	0.1682	0.1927	27.9	6.91	7.41	
	0.1942	0.2224	27.2	8.18	7.41	
	0.1641	0.1880	29.0	6.48	7.41	
			n = 6			
			mean	7.44		100.4
			std dev	0.66		
			CV_2	0.089		
1S	0.375	0.430	27.5	15.64	15.41	
	0.404	0.463	30.8	15.03	15.41	
	0.451	0.517	30.2	17.12	15.41	
	0.393	0.450	27.3	16.48	15.41	
	0.379	0.434	28.6	15.18	15.41	
	0.354	0.406	27.3	14.87	15.41	
			n = 6			
			mean	15.72		102.0
			std dev	0.90		
			CV_2	0.057		
2S	0.975	1.117	28.8	38.8	31.8	
	0.675	0.773	28.8	26.8	31.8	
	0.744	0.852	27.8	30.6	31.8	
	0.750	0.859	28.8	29.8	31.8	
	0.758	0.868	26.7	32.5	31.8	
	0.721	0.826	28.2	29.3	31.8	
			n = 6			
			mean	31.3		98.4
			std dev	4.1		
$\overline{CV}_2$	0.097		CV_2	0.131		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, ibid.

3. Documentation of NIOSH Validation Tests, ibid.

4. Backup Data Report for Methyl Cellosolve, No. S79, NIOSH Contract No. CDC-99-74-45.

Backup Data Report

Substance:	N-Ethylmorpholine, No. S146
OSHA Standard:	20 ppm (94 mg/cu m)
Chemical Used for Validation:	N-Ethylmorpholine, technical grade Union Carbide Chemicals Co.

Procedure

The procedure followed for validation of the method is essentially that of P&CAM 221. For determination of desorption efficiency, 150-mg samples of silica gel were placed in 2-ml Hewlett Packard automatic sample injector vials and were spiked with an aqueous solution containing 235 mg/ml of N-ethylmorpholine injected with a 10-microliter syringe. The amount added was 2, 4, and 8 microliters respectively for 0.5, 1, and 2 times the OSHA standard levels, and was the same as the amount present in a 10-liter air sample at the respective level. The eluting solvent was 0.1 M sulfuric acid. Silica gel tubes were supplied by SKC, Pittsburgh, Pennsylvania, Catalog No. 226-10. Gas chromatographic analyses were performed with an automatic sampler using absolute area calibration. Details of the analytical procedures are given in the Analytical Procedure section of Reference 1, except for the desorption procedure. Satisfactory desorption required ultrasonic treatment for three hours. The eluent was then decanted from the silica gel giving a yield of approximately 0.75 ml and made alkaline with 20% sodium hydroxide to pH 10-11. Basification in the presence of the silica gel produces spurious gc peaks and permits resorption of the N-ethylmorpholine.

Desorption efficiency at the 1X level was determined at one day and one week to see whether there was a significant decrease with time. Desorption efficiency samples were prepared and analyzed as described above. The desorption efficiencies were as follows:

	D.E.	CV_1
1 day (six samples)	0.883	0.058
1 week (six samples)	0.857	0.016

This difference was not considered to be significant.

Modifications

The method is similar to that described in P&CAM 221. Some differences were as follows:

1. A different size and type of silica gel tube was used. The mesh size of the silica gel was also different.

2. 0.1 M sulfuric acid instead of 0.5 M sulfuric acid was used for desorption. The amount of acid used for desorption was also different from the amount used in P&CAM 221.

3. 0.25 M sodium hydroxide instead of 1.1 M sodium hydroxide was used.

4. Ultrasonic treatment of the samples was needed for adequate desorption.

Generation

The test atmosphere was generated by a syringe-injection technique. Simultaneous three-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 22.6 liters per minute, and the rate of N-ethylmorpholine injection was 0.28 g/hour. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each silica gel tube.

Breakthrough

In order to test the capacity of the silica gel tubes, an experiment was conducted at 2X the OSHA standard level (actual concentration was 206 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5% of the concentration in the test gas mixture. In order to meet the requirement for the volume of sample to be used, it is necessary that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. Eight tubes were used to sample the test air, which was pumped through the eight tubes simultaneously through individual critical orifices. The concentration was too low to monitor, so the breakthrough experiment was run for four hours, and the backup section of the silica gel tubes analyzed for N-ethylmorpholine. Breakthrough did not occur, i.e., no N-ethylmorpholine was found in the backup section. Thus, the capacity of the silica gel exceeds 9.9 mg of N-ethylmorpholine and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Discussion

After desorbing the analyte from the silica gel, the 0.1 M sulfuric acid solution was decanted into a small glass ampule to separate the liquid phase from the bulk of the silica gel. Approximately 0.75 ml of aqueous solution was recovered. To this solution, 50 microliters of 20% by weight solution of sodium hydroxide in water was added to give a solution with a pH of 10-11. It should be noted that the uncertainty in the final concentration resulting from the addition

of 50 microliters of base to approximately 0.75 ml of solution is probably no more than 2% and was therefore, ignored in the treatment of data in this report since a similar addition of base was made to 1.0-ml aliquots of standard solutions used for calibration tests. It is important, however, that the same technique was used for standards and collected samples to avoid a serious bias in the results. Because of this ambiguity in the validation procedure it was decided that a 0.5-ml aliquot of the acid solution above the silica gel should be pipetted into a vial for the GC analysis and 0.5 ml of 0.25 M aqueous sodium hydroxide should be added to make the solution up to exactly 1 ml with a pH greater than 11. This modification is provided in the sampling and analytical method.

Precision and Accuracy

The statistical procedures are described in Reference 3.

$$\overline{CV}_1 = 0.039 \qquad \overline{CV}_2 = 0.086 \qquad \overline{CV}_T = 0.101$$

The average recovery of the generated samples at the 1X OSHA standard level was 106.2%.

Data Sheet: N-Ethylmorpholine S146

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.470	0.391	0.832	0.940	0.811	0.863	1.880	1.622	0.863
0.470	0.403	0.857	0.940	0.765	0.814	1.880	1.653	0.879
0.470	0.402	0.855	0.940	0.809	0.861	1.880	1.609	0.856
0.470	0.418	0.889	0.940	0.825	0.878	1.880	1.592	0.847
0.470	0.424	0.902	0.940	0.867	0.922	1.880	1.590	0.846
0.470	0.414	0.881	0.940	0.901	0.959	1.880	1.562	0.831
n =		6			6			6
mean		0.869			0.883			0.854
std dev		0.026			0.051			0.016
CV_1		0.030			0.058			0.019

$\overline{CV}_1$ 0.039

$\overline{CV}_{A+\overline{DE}}$ 0.042

An average D.E. of 0.869 was used for calculation of Sampling and Analysis data at all three levels on the next page.

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Data Sheet: N-Ethylmorpholine S146

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.503	0.579	10.85	53.4	56.7	
	0.502	0.578	9.70	59.6	56.7	
	0.502	0.578	9.40	61.5	56.7	
	0.410	0.472	9.30	50.8	56.7	
	0.428	0.493	9.60	51.4	56.7	
	0.494	0.568	10.35	54.9	56.7	
			n = 6			
			mean	55.3		97.5
			std dev	4.4		
			CV_2	0.080		
1S	0.958	1.102	9.15	120.4	108.7	
	1.035	1.191	10.25	116.2	108.7	
	1.125	1.295	10.05	128.9	108.7	
	0.977	1.124	9.10	123.5	108.7	
	0.817	0.940	9.55	98.4	108.7	
	0.829	0.954	9.10	104.8	108.7	
			n = 6			
			mean	115.4		106.2
			std dev	11.6		
			CV_2	0.101		
2S	1.846	2.124	9.60	221.2	206.5	
	1.779	2.047	9.60	213.2	206.5	
	1.933	2.224	9.25	240.4	206.5	
	1.929	2.220	9.60	231.2	206.5	
	1.531	1.762	8.90	198.0	206.5	
	1.666	1.917	9.40	203.9	206.5	
			n = 6			
			mean	218.0		105.6
			std dev	16.2		
$\overline{CV}_2$	0.086		CV_2	0.074		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report for Camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report for Ethyl Alcohol, No. S56, NIOSH Contract No. CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

4. Backup Data Report for Methyl Cellosolve, No. S79, NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Isopropylamine, No. S147
OSHA Standard:	5 ppm (12 mg/cu m)
Chemical Used for Validation:	Isopropylamine Matheson, Coleman, and Bell

Procedure

The procedure followed for validation of the method for collecting isopropylamine in air and measuring its concentration is described in NIOSH Method S147. The method is a combination of bubbler collection and gas chromatographic analysis of the collected samples. Isopropylamine is collected in 10 ml of 0.05 M sulfuric acid. The resulting solution is made alkaline with 4 M sodium hydroxide and an aliquot is gas chromatographed. Samples of isopropylamine in air were generated by the procedure described below and collected in midget bubblers. The "found" concentrations of isopropylamine in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 100 minutes). With an isopropylamine concentration of 21.5 mg/cu m, analysis of the solution in the backup bubbler gave negative results with a detection limit of 0.1 mg/cu m. Thus, the collection efficiency in a single bubbler is 1.00.

Generation

Isopropylamine was introduced into an air stream with an automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe filled with isopropylamine was placed in the syringe drive mechanism. The syringe, which was attached to a 15-in long stainless steel needle, delivered the analyte at a rate of approximately 1.97 μg/min into a glass tube. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.6 liters/min and diluted with air at a rate of 38.1 liters/min to obtain a concentration of approximately two times the OSHA standard. Further dilutions with air were made to obtain two lower concentrations. The dilution system is described in Reference No. 1.

A set of six samples at each of three concentrations was generated and analyzed. The analyte concentrations were different than expected. Some of the analyte was apparently lost in the generator. This being the case, the "true" concentration at the three levels could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates, and it was assumed that isopropylamine is collected with an efficiency of 1.00 as determined by the collection efficiency tests.

Samples were collected for 100 minutes at a flow rate of approximately 1 liter per minute (individual critical orifices vary slightly in flow rate).

Collection Efficiency

Collection efficiency experiments were performed at 21.51 mg/cu m at a flow rate of 1 liter per minute to test the ability of a single midget bubbler to trap the isopropylamine vapors. Six sets of two midget bubblers in series, each containing 10 ml of the collection medium, were used in these tests. The gas stream emitted from the front bubbler was bubbled through a second bubbler. Thus, any isopropylamine vapor not collected in the front bubbler would be subjected to collection in the second bubbler, allowing determination of the collection efficiency of the front bubbler. The front and backup bubbler solutions were analyzed. No isopropylamine was detected in the backup bubblers at a detection limit of 0.1 mg/cu m.

Storage Stability

To assess the stability of isopropylamine in 0.05 M sulfuric acid solution, a time study was conducted. Six samples of 10 ml of 0.05 M sulfuric acid in 25-ml volumetric flasks were spiked with isopropylamine at 1X the OSHA standard level. The samples were analyzed immediately and after 5 days. No sample loss was found.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.060$ $\overline{CV}_2 = 0.038$ $\overline{CV}_T = 0.067$

Data Sheet: Isopropylamine S147

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.600	0.530	0.883	1.200	1.272	1.060	2.400	2.336	0.973
0.600	0.671	1.118	1.200	1.254	1.045	2.400	2.401	1.000
0.600	0.595	0.992	1.200	1.210	1.008	2.400	2.279	0.950
0.600	0.618	1.030	1.200	1.188	0.990	2.400	2.476	1.032
0.600	0.566	0.943	1.200	1.101	0.918	2.400	2.375	0.990
0.600	0.620	1.033	1.200	1.175	0.979	2.400	2.534	1.056
n =		6			6			6
mean		1.000			1.000			1.000
std dev		0.081			0.051			0.039
CV_1		0.081			0.051			0.039

$\overline{CV}_1$ 0.060

$\overline{CV}_{A+\overline{AMR}}$ 0.065

Data Sheet: Isopropylamine S147

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.790	90.0	8.78
	0.790	88.9	8.89
	0.797	89.1	8.94
	0.838	96.6	8.67
	0.780	89.3	8.73
	0.839	91.3	9.41
		n = 6	
		mean	8.90
		std dev	0.27
		CV_2	0.030
1S	1.395	97.8	14.26
	1.462	93.2	15.69
	1.359	92.6	14.68
	Orifice malfunctioned		
	1.238	89.1	13.90
	1.433	92.4	15.51
		n = 5	
		mean	14.81
		std dev	0.78
		CV_2	0.053
2S	1.925	89.1	21.60
	Orifice malfunctioned		
	2.041	97.8	20.87
	1.953	92.6	21.09
	2.078	93.2	22.30
	2.004	92.4	21.69
		n = 5	
		mean	21.51
		std dev	0.56
$\overline{CV}_2$ 0.038		CV_2	0.026

* All values have passed the Grubbs outlier test at the 1% confidence level as described in Reference No. 3.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Monomethyl Hydrazine, No. S149
OSHA Standard:	0.2 ppm (0.35 mg/cu m) - skin (Ceiling)
Chemicals Used for Validation:	Monomethyl Hydrazine and Methylhydrazine Sulfate Aldrich Chemical Company

Procedure

The procedure validated for collecting and analyzing monomethyl hydrazine in air is described in NIOSH Method S149. The analysis is based on the colorimetric molybdenum blue method described in Reference No. 1. Standard samples were prepared and a standard curve was constructed by plotting absorbance versus mg of monomethyl hydrazine. Samples of monomethyl hydrazine were generated as described below and collected in midget bubblers (impingers fitted with fritted glass tipped inlet tubes) containing 15 ml of 0.1 M hydrochloric acid. Collection efficiency tests were done at 1.74 mg/cu m. The amounts of monomethyl hydrazine found (mg) in the generated samples were determined from a standard curve. The concentrations of monomethyl hydrazine in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 15 minutes).

Modification of Reference 1

The intensity of the developed color was determined at 730 nm using a Cary Model 14 M spectrophotometer with either an IR source or a tungsten lamp; both sources gave identical absorbance readings at 730 nm. Methylhydrazine sulfate was used as the standard for the calibration curve.

Analysis

Monomethyl hydrazine is slowly air-oxidized and is difficult to maintain in known purity. The validation of the analytical method and a calibration curve were therefore based on methylhydrazine sulfate. The standards were prepared in dilute hydrochloric acid, because standards prepared in water are unstable and must be prepared fresh daily. A time study indicated that the collected samples in dilute hydrochloric acid could be stored at room temperature as long as five days in a stoppered container before analysis with no loss. Six samples at the 1X OSHA level were prepared by spiking an appropriate amount of standard solution of monomethyl hydrazine in 0.1 M hydrochloric acid (1.027 mg/ml) into 15 ml of 0.1 M hydrochloric acid. The five day results are given on the next page.

TIME STUDY OF MONOMETHYL HYDRAZINE AFTER FIVE DAYS

µg added	µg found after 5 days	% Recovery
8.21	8.37	102.0
8.21	8.18	99.6
7.90	8.09	102.4
7.90	8.34	105.6
8.07	8.79	108.9
8.07	8.73	108.2
	mean	104.4

The results for immediate analysis are given at the 1S level in the table labelled Analysis.

Generation

Monomethyl hydrazine was introduced into an air stream with an automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe filled with monomethyl hydrazine in methanol (1 ml monomethyl hydrazine brought up to 10 ml with methanol) was placed in the syringe drive mechanism. The syringe, which was attached to a 15-in long stainless steel needle, delivered the analyte at a rate of 276.6 µg/min into a heated glass tube which was heated with a heating lamp. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.6 liters/minute and diluted with air at a rate of 167.9 liters/minute to obtain a concentration of approximately two times the OSHA standard. The actual concentration in the generator was considerably lower than that predicted from the above data. Further dilutions with air were made to obtain two lower concentrations. The dilution system is described in Reference No. 2.

A set of six samples at each of three concentration levels were generated and analyzed. The "true" concentration at the three levels could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates. The reason for this is unknown. It may be due to instability of monomethyl hydrazine due to oxidation and decomposition upon contact with the atmosphere (Reference No. 3). Samples were collected for 15 minutes at approximately 1.5 liters per minute.

Collection Efficiency

The collection efficiency was determined by connecting two bubblers in series at each of six sampling ports. The collection efficiency experiments were conducted at a concentration of 1.808 mg/cu m (as determined by analysis of the front and backup bubblers) in order to give a high enough reading in the backup bubbler if 5% of the generated concentration broke through. The results are given on the next page.

First Bubbler (mg/cu m)	Backup Bubbler (mg/cu m)	Collection Efficiency (%)
1.718	0.088	95.1
1.770	-0-	100.0
1.737	0.028	98.4
1.739	0.091	95.0
1.823	0.076	96.0
1.685	0.094	94.7
	mean	96.5
	std dev	2.2

The collection efficiency in a single bubbler was sufficient so it was not considered appropriate to apply a collection efficiency correction.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.029$ $\overline{CV}_2 = 0.093$ $\overline{CV}_T = 0.106$

Data Sheet: Monomethyl Hydrazine S149

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
3.94	4.19	1.064	8.20	8.34	1.017	16.08	16.15	1.004
3.94	4.26	1.081	8.20	9.05	1.104	16.08	16.25	1.011
3.79	3.93	1.037	7.90	7.98	1.010	15.49	15.54	1.003
3.79	4.06	1.071	7.90	7.92	1.002	15.49	14.60	0.942
3.87	3.93	1.016	8.07	8.24	1.021	15.82	15.66	0.990
3.87	4.03	1.041	8.07	8.50	1.053	15.82	15.80	0.999
n =		6			6			6
mean		1.052			1.034			0.992
std dev		0.024			0.038			0.025
CV_1		0.023			0.037			0.025

$\overline{CV}_1$ 0.029

$\overline{CV}_{A+\overline{AMR}}$ 0.031

Data Sheet: Monomethyl Hydrazine S149

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	3.52	21.18	0.1662
	3.96	21.56	0.1837
	4.25	21.81	0.1949
	3.52	20.00	0.1760
	3.52	22.50	0.1564
	2.84	20.69	0.1373
		n = 6	
		mean	0.1691
		std dev	0.020
		CV_2	0.118
1S	9.40	20.46	0.459
	8.28	20.69	0.400
	8.57	21.06	0.407
	10.10	21.06	0.480
	10.10	21.06	0.480
	9.59	22.79	0.421
		n = 6	
		mean	0.441
		std dev	0.036
		CV_2	0.082
2S	17.80	20.69	0.860
	15.08	21.81	0.691
	17.74	21.56	0.823
	16.11	21.18	0.761
	15.57	20.00	0.778
	17.77	22.50	0.790
		n = 6	
		mean	0.784
		std dev	0.058
$\overline{CV}_2$ 0.093		CV_2	0.074

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. L. Feinsilver, J. A. Perregrino, and C. J. Smith, Jr., "Estimation of Hydrazine and Three of Its Methyl Derivatives," Industrial Hygiene Journal, 20, February 1959, 26-31.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Thomas Dambrauskas and Herbert H. Cornish, "A Modified Spectrophotometric Method for the Determination of Hydrazine," Industrial Hygiene Journal, March-April, 1962, 151.

4. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Morpholine, No. S150
OSHA Standard:	20 ppm (70 mg/cu m) - skin
Chemical Used for Validation:	Morpholine, 99%+ Aldrich Chemical

Procedure

The procedure for collecting and analyzing concentrations of morpholine in air is described in NIOSH Method S150, which has been adapted from P&CAM 221. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of morpholine to represent 20-liter air samples. Samples of morpholine were generated by a syringe drive injection and air dilution system and collected in silica gel tubes. The analyte was desorbed with 0.05 M sulfuric acid. The desorbed sample was made alkaline with 1.2 M sodium hydroxide and analyzed by gas chromatography. The amounts measured were corrected for desorption efficiency (D.E.) to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 110 minutes). The collection efficiency of the silica gel tubes was found to be 1.00, because analysis of the backup sections of the silica gel tubes did not show the presence of morpholine at a detection limit of 0.035 mg/cu m.

Modifications

The method is similar to that described in P&CAM 221. Some differences were as follows:

1. A different size and type of silica gel tube was used. The mesh size of the silica gel was also different.

2. 0.05 M sulfuric acid instead of 0.5 M sulfuric acid was used for desorption. The amount of acid used for desorption was also different from the amount used in P&CAM 221.

3. 1.2 M sodium hydroxide instead of 1.1 M sodium hydroxide was used.

4. A solution of morpholine in hexane containing 350 mg/ml was used to apply the analyte to the silica gel for desorption efficiency tests, so it would not be necessary to inject less than 2 µl at the 0.5X level.

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* Silica gel tubes were obtained from Environmental Compliance Corp.

Generation

Samples of morpholine were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with morpholine and placed in the syringe drive mechanism. The syringe, which was attached to a 15-in long stainless steel needle, delivered the analyte at a rate of 3.78 mg/min into a glass tube, which was heated with a heating lamp. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.7 liters/min and diluted with air at a rate of 23.12 liters/min to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X level. The dilution system is described in Reference No. 1.

A set of six samples at each of the three levels (2X, 1X, and 0.5X the OSHA standard) were generated and analyzed. The concentrations of these samples were lower than expected, so a second set of samples at each of the three levels was generated. A possible explanation for the low values of the first generated samples is that morpholine could have been destroyed in the heated oven. Therefore, during the second generation, the output of the generator was maximized by varying the amount of heat that was applied to the oven and obtaining a maximum response on the total hydrocarbon analyzer. The concentration of six samples at each level was again found to be low. It is assumed that the cause of the low values was due to loss of morpholine in the generator. This being the case, the "true" concentration at the 2X, 1X, and 0.5X OSHA standard level could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates.

Samples were collected for 110 minutes at a flow rate of approximately 0.2 liter per minute.

Collection Efficiency

Collection efficiency tests were conducted at 108.4 mg/cu m by analyzing the backup sections of the silica gel tubes. The results are given in the table on the following page.

mg/cu m in front section	mg/cu m in backup	C.E.
107.2	N.D.*	1.00
108.5	N.D.	1.00
111.1	N.D.	1.00
109.3	N.D.	1.00
108.5	N.D.	1.00
105.5	N.D.	1.00

* Not detected. Limit of detection is 0.035 mg/cu m.

Breakthrough

A breakthrough test of the front section of silica gel tubes was conducted as described in Reference No. 2. The two-piece glass generator described in Reference No. 3 was used for the breakthrough test. The glass generator was immersed in a water bath at 25°C. The flow of nitrogen through the generator was 0.1 liter per minute and dilution air flow rate was 44.4 liters per minute. The breakthrough test was conducted at a concentration of 135 mg/cu m. This concentration was determined by relating the response of the total hydrocarbon analyzer during the breakthrough test to the response of the hydrocarbon analyzer during sample generation, using the concentration of the analyzed samples at the 2X level. Less than 5% of the generated concentration of 135 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.2 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

The original method recommended for morpholine was P&CAM 127 which is collection of the analyte on charcoal and desorption with a suitable desorbing solvent. Desorption efficiency tests for morpholine on charcoal Lot 105 at the 1X OSHA level were conducted. One hundred mg of charcoal was spiked with 4 µl of a hexane solution of morpholine containing 350 mg/ml. Desorption was done using 1 ml of 95% ethanol for 30 minutes. Analysis was done by gas chromatography with hydrogen flame ionization detection.

A 4-ft by 1/4-in stainless steel column packed with 80/100 mesh Chromosorb 103 was used. The column temperature was 100°C, the detector temperature was 270°C, and the injection temperature was 235°C. The results of the D.E. tests are given below:

mg taken	mg found	D.E.
1.400	0.662	0.473
1.400	0.676	0.483
1.400	0.682	0.487
1.400	0.646	0.461
1.400	0.634	0.453
1.400	0.636	0.454
	mean	0.468

Because of the low recoveries of the above D.E. test, another set of D.E.'s were run on charcoal Lot 105, using ethyl ether as the desorbing solvent. The samples were spiked in the same manner as done above, and the same GC conditions were used. The results are given below:

mg taken	mg found	D.E.
1.400	0.408	0.291
1.400	0.367	0.262
1.400	0.327	0.234
1.400	0.410	0.293
1.400	0.328	0.234
1.400	0.362	0.258
	mean	0.262

Because of the poor recoveries on charcoal, desorption from 20/40 mesh silica gel was tried. Spiking was done as before using 4 µl aliquots of the solution of morpholine in hexane containing 350 mg/ml. This solution was used to spike 150-mg portions of silica gel. Desorption was done using 1 ml of 95% ethanol for 1 hour in an ultrasonic bath. The same GC conditions described above were used. The results of the D.E. tests are given on the next page.

mg taken	mg found	D.E.
1.400	0.468	0.334
1.400	0.389	0.278

Another set of desorption efficiencies on silica gel was repeated as above, only ethyl ether was used as the desorbing solvent. There was no response on the gas chromatogram.

Another set of D.E.'s on silica gel was again conducted, using acid desorption. Again 4 µl of the morpholine solution in hexane containing 350 mg/ml was used to spike 150-mg portions of 20/40 mesh silica gel. Morpholine was desorbed from the silica gel with 1 ml of 0.05 M sulfuric acid for 30 minutes. The solution was made alkaline with 150 µl of 1.2 M sodium hydroxide. The peaks were very broad. the results are given below:

mg taken	mg found	D.E.
1.400	0.670	0.478
1.400	0.832	0.594
	mean	0.536

Another set of silica gel tubes were spiked as previously done above, and were desorbed for 30 minutes with 1 ml 0.05 M sulfuric acid. This time an aliquot of 0.5 ml of the desorbed sample was transferred to a fresh vial and 50 µl of 1.2 M sodium hydroxide was added to make the solution alkaline. The peaks on the gas chromatogram were much larger than before. Taking an aliquot of the desorbed sample, before adding the base, apparently prevents morpholine from adhering to the silica gel. The results of the above test are given below:

mg taken	mg found	D.E.
1.400	1.289	0.921
1.400	1.233	0.881
	mean	0.901

Since the above D.E.'s were satisfactory, it was decided to use the technique of taking an aliquot of the desorbed sample before adding the base. An Ascarite "precolumn" in front of the Chromosorb 103 column eliminated the broad peaks which were observed when no Ascarite was used. Desorption efficiencies for each of the three levels were measured and the results are given in the Analysis table.

The GC conditions used were as follows:

1. 4-ft x 1/4" stainless steel column backed with 80/100 mesh Chromosorb 103. A 3-in Ascarite precolumn was inserted at the inlet end of the column and was separated from the Chromosorb packing by a plug of glass wool.

2. Column Temperature = 190°C

3. Detector Temperature = 280°C

4. Injection Temperature = 250°C

A time study was conducted to determine the recovery of morpholine on silica gel when added from a vapor phase. Six samples at each of the three OSHA levels were generated using the syringe drive pump as described under the Generation Section. The 0.5X level samples were lost due to malfunction of the gas chromatograph during analysis. Three samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the silica gel tubes. The samples were allowed to stand for one week before analysis. The samples were desorbed with 0.05 M sulfuric acid. A 0.5 ml aliquot of the desorbed samples was transferred to a fresh vial and 50 µl of 1.2 M sodium hydroxide was added to make the solution alkaline. The results are given below:

TIME STUDY RESULTS OF MORPHOLINE

(FLUSHED WITH NITROGEN)

	mg found	corr. mg	Liters		mg/cu m
2X	1.90	2.03	18.48		109.9
	2.08	2.22	20.57		107.9
	1.94	2.07	19.80		104.6
				mean	107.5
1X	0.905	0.969	19.03		50.9
	0.886	0.950	16.94		56.1
	0.971	1.038	18.81		55.2
				mean	54.1

(NOT FLUSHED WITH NITROGEN)

2X	1.94	2.07	20.46		101.2
	1.95	2.08	20.24		102.8
	1.87	2.00	19.47		102.7
				mean	102.2
1X	0.943	1.010	19.14		52.8
	0.915	0.980	18.37		53.3
	0.924	0.989	19.47		50.8
				mean	52.3

The corr. mg in the above table was calculated by using the D.E. equation in the Analysis table at the end of this report.

From the above results, morpholine is adequately stable on silica gel for at least one week without flushing with nitrogen. These results were compared with the data in the Sampling and Analysis Table which represents the samples that were analyzed immediately after generation.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.026$ $\overline{CV}_2 = 0.025$ $\overline{CV}_T = 0.057$

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Data Sheet: Morpholine S150

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.700	0.632	0.903	1.400	1.262	0.901	2.100	1.905	0.907
0.700	0.661	0.944	1.400	1.291	0.922	2.100	2.022	0.963
0.700	0.640	0.914	1.400	1.275	0.911	2.100	2.021	0.962
0.700	0.668	0.954	1.400	1.331	0.951	2.100	1.969	0.938
0.700	0.620	0.886	1.400	1.345	0.961	2.100	2.024	0.964
0.700	0.652	0.931	1.400	1.291	0.922	2.100	1.950	0.929

n =	6	6	6
mean	0.922	0.928	0.944
std dev	0.026	0.023	0.023
CV_1	0.028	0.025	0.024

$\overline{CV}_1$ 0.026

$\overline{CV}_{A+\overline{DE}}$ 0.028

The equation D.E. = $0.937 - e^{-6.31 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 5.

Data Sheet: Morpholine S150

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.552	0.613	21.12	29.0
	0.581	0.638	22.11	28.9
	0.597	0.653	22.77	28.7
	0.522	0.580	21.89	26.5
	0.557	0.614	21.12	29.1
	0.534	0.591	20.68	28.6
			n = 6	
			mean	28.5
			std dev	1.0
			CV_2	0.035
1S	1.023	1.094	19.03	57.5
	0.926	0.991	16.94	58.5
	1.015	1.086	18.37	59.1
	1.002	1.072	18.81	57.0
	1.060	1.134	19.47	58.2
	Sample was lost.			
			n = 5	
			mean	58.1
			std dev	0.8
			CV_2	0.014
2S	1.857	1.982	18.48	107.2
	2.091	2.232	20.57	108.5
	2.130	2.273	20.46	111.1
	2.073	2.212	20.24	109.3
	2.014	2.149	19.80	108.5
	1.925	2.054	19.47	105.5
			n = 6	
			mean	108.4
			std dev	1.9
$\overline{CV}_2$ 0.025			CV_2	0.018

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Triethylamine, No. S152
OSHA Standard:	25 ppm (100 mg/cu m)
Chemical Used for Validation:	Triethylamine Matheson, Coleman, and Bell

Procedure

The procedure followed for validation of the method for collecting triethylamine in air and measuring its concentration is described in NIOSH Method S152. The method is a combination of midget bubbler collection and gas chromatographic analysis of the collected samples. Triethylamine is collected in 10 ml of 0.05 M sulfuric acid. The resulting solution is made alkaline with 4 M sodium hydroxide, and an aliquot is gas chromatographed. Samples of triethylamine in air were generated by the procedure described below and collected in midget bubblers. The "found" concentrations of triethylamine in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 100 minutes). For a triethylamine concentration of 193 mg/cu m in the air stream entering the front midget bubbler, no triethylamine was detected in the backup midget bubbler with a detection limit of 0.5 mg/cu m. Thus, the collection efficiency in a single bubbler is 1.00.

Generation

Samples of triethylamine were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-in long stainless steel needle was attached to the syringe. The needle passed through a rubber septum with the end in a heated glass tube. The syringe drive pump delivered 5.5 mg/min of triethylamine into the tube. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.6 liters/min, and it was diluted with air at a rate of 19.9 liters/min immediately downstream from the heated zone to obtain the 2X OSHA level. The 2X chamber was monitored with the hydrocarbon analyzer during sampling. Additional dilutions were made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. Samples were collected for 110 minutes at a rate of approximately 1 liter per minute.

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using the rate of delivery of the syringe drive and the flow rates of the dilution air. These concentrations were monitored for constancy with a total hydrocarbon analyzer. The

2X samples were found to be lower than expected. It was found that the 2X chamber dilution system was not operating properly. Also two orifices at this level were not functioning properly. Analysis of the 1X and 0.5X samples showed that the "found" concentration at these levels were close to the "taken" concentration. Therefore, a second attempt was made to generate six samples of triethylamine at the 2X level. The two-piece vapor generator described in Reference No. 2 was used. The vapor generator was set in a water bath maintained at 25°C and the nitrogen and air flow rates were adjusted to give an appropriate vapor concentration. Four bag standards were used to calibrate a Beckman 402 total hydrocarbon analyzer which was used to monitor the 2X chamber during sampling (Reference No. 3). Samples were collected for 110 minutes at a rate of approximately 1 liter per minute. Analyses of the six samples were made and the "found" concentrations were satisfactory. Thus, the 2X samples of the second generation and the 0.5 and 1X samples of the first generation were used for the statistical analysis and are reported at the end of this report.

Collection Efficiency

Collection efficiency experiments were performed at 193 mg/cu m (2X OSHA level as determined by a bag standard as described above) to test the ability of a single midget bubbler to trap the triethylamine vapors. Six sets of two midget bubblers in series, each containing 10 ml of the collection medium, were used in these tests. The gas stream emitted from the front bubbler was bubbled through a second bubbler. Thus, any triethylamine vapor not collected in the front bubbler would be subjected to collection in the second bubbler, allowing determination of the collection efficiency of the front bubbler. The front and backup bubbler solutions were analyzed. No triethylamine was detected in the backup bubblers at a detection limit of 0.5 mg/cu m.

Storage Stability

To assess the stability of triethylamine in 0.05 M sulfuric acid solution, a time study was conducted. Six samples of 10 ml of 0.05 M sulfuric acid in 25-ml volumetric flasks were spiked with triethylamine at the 1X OSHA standard level. The samples were analyzed immediately and after 5 days. No concentration changes were found.

Discussion

Preliminary work on triethylamine was conducted using 20/40 mesh acid treated silica gel. The acid treated silica gel was prepared as described in Reference 4. Four microliters of triethylamine in hexane (500 mg/ml) was used to spike the acid treated silica gel. The analyte was desorbed from the silica gel in an ultrasonic bath for 0.5 hour with 1 ml distilled water, and a 0.5-ml aliquot of the resulting solution was made alkaline with 0.5 ml 1 M sodium hydroxide.

The desorption efficiency was found to be 0.73, using the following GC conditions:

1. Column (6 ft long X 1/4 in O.D. glass) packed with 4% Carbowax 20M and 0.8% KOH on Carbopak B. A 3-in Ascarite "precolumn" is inserted at the inlet end of the column.

2. Column temperature is 135°C.

Increasing the desorption time to one hour in an ultrasonic bath did not increase the recovery of triethylamine from the acid treated silica gel. Because of the poor recoveries using water desorption, desorption in dilute sulfuric acid was tried. Both 20/40 mesh acid treated silica gel and untreated 20/40 mesh silica gel was tried. The same GC conditions as above were used, and the samples were spiked onto the silica gel in the same manner as described above. The results are given below:

DESORPTION EFFICIENCY OF TRIETHYLAMINE FROM ACID TREATED SILICA GEL

	Desorption Efficiency (Average of two samples)
Desorbed from silica gel with 1 ml 0.5M sulfuric acid for 1 hour in an ultrasonic bath. A 0.5-ml aliquot of the resulting solution is made alkaline with 0.5-ml 4 M sodium hydroxide.	0.602
Desorbed from silica gel with 1 ml 0.05 M sulfuric acid for 1 hour in an ultrasonic bath. A 0.5-ml aliquot of the resulting solution is made alkaline with 0.5-ml 4 M sodium hydroxide.	0.576

DESORPTION EFFICIENCY OF TRIETHYLAMINE FROM UNTREATED SILICA GEL

	Desorption Efficiency (Average of two samples)
Desorbed from silica gel with 1 ml of 0.05M sulfuric acid for one hour in an ultrasonic bath. A 0.5-ml aliquot of the resulting solution is made alkaline with 0.5-ml 0.1 M sodium hydroxide.	0.709
Desorbed from silica gel with 1 ml of 0.5 M sulfuric acid for one hour in an ultrasonic bath. A 0.5-ml aliquot of the resulting solution is made alkaline with 0.5-ml 2 M sodium hydroxide.	0.664

Because of the poor D.E.'s using the acid treated silica gel and the untreated silica gel, it was decided to choose another method of sampling for triethylamine. Midget bubbler collection of triethylamine in 10 ml 0.05 M sulfuric acid, followed by GC analysis of a 0.5-ml aliquot of the collected sample, which was made alkaline with 4 M sodium hydroxide, was tried and proved to be satisfactory.

Precision and Accuracy

The statistical procedures used are described in Reference No. 5.

$\overline{CV}_1 = 0.029$ $\overline{CV}_2 = 0.039$ $\overline{CV}_T = 0.064$

The average recovery at the OSHA standard level was 94.4%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Triethylamine S152

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
5.06	5.04	0.996	10.12	9.73	0.961	20.24	19.29	0.953
5.06	5.00	0.988	10.12	10.19	1.007	20.24	20.24	1.000
5.06	5.04	0.996	10.12	10.32	1.020	20.24	19.04	0.941
5.06	5.04	0.996	10.12	10.04	0.992	20.24	20.69	1.022
5.06	5.12	1.012	10.12	10.12	1.000	20.24	21.14	1.045
5.06	5.12	1.012	10.12	10.31	1.019	20.24	21.09	1.042
n =		6			6			6
mean		1.000			1.000			1.000
std dev		0.010			0.022			0.045
CV_1		0.010			0.022			0.045

$\overline{CV}_1$ 0.029

$\overline{CV}_{A+\overline{AMR}}$ 0.031

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Data Sheet: Triethylamine S152

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	4.90	106.5	46.0	50.0	
	4.72	99.2	47.6	50.0	
	4.67	100.0	46.7	50.0	
	4.74	93.0	51.0	50.0	
	4.91	102.3	48.0	50.0	
	5.09	100.4	50.7	50.0	
		n = 6			
		mean	48.3		96.6
		std dev	2.1		
		CV_2	0.043		
1S	9.53	102.0	93.4	100.0	
	8.75	88.0	99.4	100.0	
	8.30	96.4	86.1	100.0	
	9.16	94.9	96.5	100.0	
	9.30	96.4	96.5	100.0	
	Sample was lost due to malfunctioning orifice.				
		n = 5			
		mean	94.4		94.4
		std dev	5.1		
		CV_2	0.054		
2S	18.85	102.5	183.9	193.0	
	18.63	100.0	186.3	193.0	
	19.47	103.3	188.5	193.0	
	19.34	103.1	187.6	193.0	
	19.22	100.8	190.7	193.0	
	20.12	108.6	185.3	193.0	
		n = 6			
		mean	187.0		96.7
		std dev	2.4		
$\overline{CV}_2$ 0.039		CV_2	0.013		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Ethylenediamine, No. S145, prepared under NIOSH Contract CDC-99-74-45.

5. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Monomethyl Aniline (N-Methylaniline), No. S153
OSHA Standard:	2 ppm (9 mg/cu m) - skin
Chemical Used for Validation:	N-Methylaniline Aldrich Chemical

Procedure

The procedure followed for validation of the method for collecting monomethyl aniline in air and measuring its concentration is described in NIOSH Method S153. The method is a combination of bubbler collection and gas chromatographic analysis of the collected samples. Monomethyl aniline is collected in 10 ml of 0.05 M sulfuric acid. The resulting solution is made alkaline with 4 M sodium hydroxide and an aliquot is gas chromatographed. Samples of monomethyl aniline in air were generated by the procedure described below and collected in midget bubblers. The "found" concentrations of monomethyl aniline in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 100 minutes). The "true" concentration at the 2X, 1X, and 0.5X standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Generation

Monomethyl aniline was introduced into an air stream with an automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe filled with monomethyl aniline was placed in the syringe drive mechanism. The syringe, which was attached to a 15-in. long stainless steel needle, delivered the analyte at a rate of 1.883 mg/min into a heated glass tube, heated with a heating lamp. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.7 liters/min and diluted with air at a rate of 99.8 liters/min to obtain a concentration of approximately 2X the OSHA standard. Further dilutions with air were made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The recovery of the generated samples at the 0.5X OSHA level was low, because of a possible leak in the dilution system. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling. Samples were collected for 100 minutes at a rate of approximately 1 liter per minute (individual critical orifices vary slightly in flow rate).

Collection Efficiency

Collection efficiency experiments were performed at 17.5 mg/cu m to test the ability of a single midget bubbler to trap the monomethyl aniline vapors. Six sets of two midget bubblers in series, each containing 10 ml of the collection medium, were used in these tests. The gas stream emitted from the front bubbler was bubbled through a second bubbler. Any monomethyl aniline vapor not collected in the front bubbler would be subjected to collection in the second bubbler, allowing determination of the collection efficiency of the front bubbler. The front and backup bubbler solutions were analyzed. No monomethyl aniline was detected in the backup bubblers at a detection limit of 0.08 mg/cu m.

Storage Stability

To assess the stability of monomethyl aniline in 0.05 M sulfuric acid solution, a time study was conducted. Six samples of 10 ml of 0.05 M sulfuric acid in 25-ml volumetric flasks were spiked with monomethyl aniline at the 1X OSHA standard level. The samples were analyzed immediately and after 7 days. No sample loss was found. The data for samples which were analyzed immediately are given in the Analysis Table at the end of this report, and the data for samples stored for 7 days are given below:

mg taken	mg found	A.M.R.
0.791	0.822	1.039
0.791	0.839	1.061
0.791	0.799	1.010
0.791	0.777	0.982
0.791	0.755	0.954
0.791	0.672	0.850
	mean	0.983
	std dev	0.075
	CV	0.077

Discussion

Initial work on monomethyl aniline was conducted using 20/40 mesh silica gel as the collection medium. A sample size of 20 liters was chosen. This necessitated collection of monomethyl aniline at a flow rate of 0.20 liter per minute for 100 minutes.

A standard stock solution of monomethyl aniline in benzene was prepared (49.4 mg/ml). This solution was used to spike 150-mg portions of silica gel for desorption efficiency tests. The monomethyl aniline was desorbed from the silica gel with 95% ethanol for one hour in an ultrasonic bath. The data are presented in Table 1. The GC conditions used are as follows:

1. Column (2 ft long by 1/8-in O.D. stainless steel), packed with 80/100 mesh Chromosorb 103.

2. Column temperature = 175°C

3. Detector temperature = 240°C

4. Inlet temperature = 230°C

Table 1

DESORPTION EFFICIENCY OF MONOMETHYL ANILINE
USING 20/40-MESH SILICA GEL

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.0988	0.0944	0.955	0.1976	0.1918	0.971	0.395	0.395	1.000
0.0988	0.0950	0.962	0.1976	0.1915	0.969	0.395	0.396	1.002
0.0988	0.0941	0.952	0.1976	0.1910	0.967	0.395	0.395	1.000
0.0988	0.1039	1.052	0.1976	0.1991	1.008	0.395	0.394	0.997
0.0988	0.0989	1.001	0.1976	0.2019	1.022	0.395	0.381	0.965
0.0988	0.0998	1.010	0.1976	0.2013	1.019	0.395	0.389	0.985
n =		6			6			6
mean		0.989			0.993			0.992
std dev		0.040			0.026			0.014
CV_1		0.040			0.026			0.014

$\overline{CV}_1$ 0.029

An average D.E. of 0.991 is used to calculate corr. mg in the Sampling and Analysis table.

Since the D.E.s were satisfactory for monomethyl aniline, generation of the analyte was conducted. The analyte was collected in 7-cm long silica gel tubes (6-mm O.D.) containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contained approximately 150 mg of silica gel and the backup section approximately 75 mg.

Samples of monomethyl aniline were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with monomethyl aniline and placed in the syringe drive pump. The syringe, which was attached to a 15-inch long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 2.01 mg/minute. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.7 liters/minute and diluted with air at a rate of 103.4 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

Samples were collected for 120 minutes at a rate of approximately 0.18 liter per minute (individual critical orifices vary slightly in flow rate).

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2 using the syringe drive pump and the same conditions described above. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 18.11 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.18 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

The data for collection of monomethyl aniline in the silica gel tubes are given in Table 2.

Table 2

Test Level	Found				Taken	
	mg	Corr mg*	Liters	mg/cu m**	mg/cu m	Recovery
0.5S	0.0903	0.0911	23.04	3.95	4.43	
	0.0926	0.0934	24.12	3.87	4.43	
	0.0970	0.0979	24.84	3.94	4.43	
	0.0927	0.0935	23.88	3.92	4.43	
	0.0929	0.0937	23.04	4.07	4.43	
	0.0820	0.0827	22.56	3.67	4.43	
			n = 6			
			mean	3.90		88.0
			std dev	0.13		
			CV_2	0.033		
1S	0.1710	0.1726	20.88	8.27	8.87	
	0.1802	0.1818	20.76	8.76	8.87	
	0.1479	0.1492	18.48	8.07	8.87	
	0.1571	0.1585	20.04	7.91	8.87	
	0.1602	0.1616	20.52	7.88	8.87	
	0.1622	0.1637	21.24	7.71	8.87	
			n = 6			
			mean	8.10		91.3
			std dev	0.37		
			CV_2	0.046		
2S	0.322	0.325	20.16	16.12	17.74	
	0.381	0.384	22.44	17.11	17.74	
	0.383	0.386	22.32	17.29	17.74	
	0.364	0.367	22.08	16.62	17.74	
	0.334	0.337	21.60	15.60	17.74	
	0.343	0.346	21.24	16.29	17.74	
			n = 6			
			mean	16.50		93.0
			std dev	0.63		
$\overline{CV}_2$ 0.039			CV_2	0.038		

* A desorption efficiency of 0.991 was used to calculate corr. mg.

** All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

A time study was conducted to determine the recovery of monomethyl aniline on silica gel when added from a vapor phase. Six samples at each of three levels were generated using the syringe drive pump as described above. Three of the samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the silica gel tubes. The samples were allowed to stand for one week before analysis. The samples were desorbed with 95% ethanol for 1 hour in an ultrasonic bath. The results are given below:

TIME STUDY RESULTS OF MONOMETHYL ANILINE

	Found				Taken	
Level	mg found	corr. mg*	Liters	mg/cu m	mg/cu m	Recovery(%)
			(FLUSHED WITH NITROGEN)			
0.5X	0.0762	0.0769	23.04	3.34	4.43	
	0.0786	0.0793	24.84	3.19	4.43	
	0.0892	0.0900	23.88	3.77	4.43	
			mean	3.43		77.4
1X	0.1332	0.1344	18.48	7.27	8.87	
	0.1491	0.1504	20.52	7.33	8.87	
	0.1169	0.1180	21.24	5.56	8.87	
			mean	6.72		75.8
2X	0.255	0.257	20.16	12.75	17.74	
	0.271	0.273	22.44	12.17	17.74	
	0.239	0.241	22.08	10.92	17.74	
			mean	11.95		67.4
			(NOT FLUSHED WITH NITROGEN)			
0.5X	0.0937	0.0946	24.12	3.92	4.43	
	0.0648	0.0654	23.04	2.84	4.43	
	0.0676	0.0682	22.56	3.02	4.43	
			mean	3.26		73.6
1X	0.1334	0.1346	20.88	6.45	8.87	
	0.1051	0.1060	20.76	5.10	8.87	
	0.1070	0.1080	20.04	5.39	8.87	
			mean	5.65		63.7
2X	0.1981	0.1999	22.32	8.96	17.74	
	0.2001	0.2019	21.60	9.35	17.74	
	0.2326	0.2347	21.24	11.05	17.74	
			mean	9.79		55.2

* A desorption efficiency of 0.991 was used to calculate corr. mg.

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Although flushing with nitrogen gave higher recoveries, the recoveries are still unsatisfactory. Because monomethyl aniline is unstable on silica gel for a period of one week, it was decided to choose another method of sampling. Midget bubbler collection of the analyte in 10 ml 0.05 M sulfuric acid, followed by GC analysis of a 0.5-ml of the collected sample, which was made alkaline with 4 M sodium hydroxide, was found to be satisfactory. The analyte is stable for at least one week in the 0.05 M sulfuric acid collection medium.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for monomethyl aniline as in Reference No. 4.

The sampling and analysis data gave a chi squared value of 9.6 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. Therefore, CV_T is calculated only on the data at the 1X level.

$$CV_T = \sqrt{CV_2^2 + (0.05)^2} = 0.089$$

Where:

CV_2 = Coefficient of Variation at the 1X level for Sampling and Analysis = 0.074

(0.05)= pump error

The average recovery at the OSHA standard level was 96.1%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, CV_T is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Monomethyl Aniline S153

Analysis

Level

mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.396	0.390	0.985	0.791	0.738	0.933	1.582	1.574	0.995
0.396	0.401	1.013	0.791	0.799	1.010	1.582	1.600	1.011
0.396	0.402	1.015	0.791	0.822	1.039	1.582	1.606	1.015
0.396	0.400	1.010	0.791	0.807	1.020	1.582	1.585	1.002
0.396	0.395	0.997	0.791	0.796	1.006	1.582	1.572	0.994
0.396	0.385	0.972	0.791	0.786	0.994	1.582	1.557	0.984

n =	6	6	6
mean	0.999	1.000	1.000
std dev	0.017	0.036	0.012
CV_1	0.017	0.036	0.012

$\overline{CV}_1$ 0.024

$\overline{CV}_{A+\overline{AMR}}$ 0.026

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Data Sheet: Monomethyl Aniline S153

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.292	96.4	3.03	4.38	
	0.294	84.5	3.48	4.38	
	0.391	96.6	4.05	4.38	
	0.384	94.6	4.06	4.38	
	0.325	95.5	3.40	4.38	
	0.343	89.3	3.84	4.38	
		n = 6			
		mean	3.64		83.1
		std dev	0.41		
		CV_2	0.112		
1S	0.720	90.0	8.00	8.76	
	0.802	88.9	9.02	8.76	
	0.739	89.1	8.29	8.76	
	0.727	96.6	7.53	8.76	
	0.821	89.3	9.19	8.76	
	0.773	91.3	8.47	8.76	
		n = 6			
		mean	8.42		
		std dev	0.62		96.1
		CV_2	0.074		
2S	1.766	97.8	18.06	17.52	
	1.639	92.6	17.70	17.52	
	* 1.213	89.1	13.61	17.52	
	1.635	92.4	17.70	17.52	
	1.635	93.2	17.54	17.52	
	1.566	90.5	17.30	17.52	
		n = 5			
		mean	17.66		100.8
		std dev	0.28		
$\overline{CV}_2$ 0.081		CV_2	0.016		

* These numbers did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Tetramethyl Succinonitrile, No. S155

OSHA Standard: 0.5 ppm (3 mg/cu m) - skin

Chemical Used for Validation: Tetramethyl Succinonitrile
Chemical Samples Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of tetramethyl succinonitrile in air is described in NIOSH Method S155, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of tetramethyl succinonitrile to represent 50-liter air samples. Laboratory generated samples of tetramethyl succinonitrile in air were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The analyte was desorbed with carbon disulfide. Analysis was by gas chromatography. The results were corrected for desorption efficiency. The "found" concentrations of tetramethyl succinonitrile in air were determined by dividing the corrected mg found by the volume sampled (critical orifice flow rate for that sample X 60 minutes). It was not possible to determine the "true" concentration in the generation system. However, it was possible to monitor the stability of the concentration levels at the three OSHA standard levels using a total hydrocarbon analyzer.

Modifications

One major modification of P&CAM 127 was made. A 20% (V/V) acetone-hexane solution of tetramethyl succinonitrile (34.75 mg/ml) was used to apply the analyte to the charcoal. The reason for this modification is discussed in the Discussion Section of this report.

Generation

A literature search provided no useful data on the vapor pressure of tetramethyl succinonitrile below its melting point to assist in defining conditions for the generation of the desired levels.

The sensitivity on the Beckman Model 402 total hydrocarbon analyzer was sufficient to monitor the concentration level in the generation system, but there was no method of determining what concentration levels of tetramethyl succinonitrile vapor were being generated. Assuming a similar response for iso-octane and tetramethyl succino-nitrile (both compounds have eight carbons) on the flame ionization detector of the total hydrocarbon analyzer, it should be theoretically

possible to make a bag standard of iso-octane for purposes of calibrating the generation of tetramethyl succinonitrile. A bag standard of iso-octane was prepared at 556 mg/cu m (8.7 ml/10 liters air). This corresponds to a concentration level of 200 times the OSHA standard for tetramethyl succinonitrile. The linear response of the electrometer on the total hydrocarbon analyzer allowed the establishment of generator conditions which would approximately give the three desired concentration levels for tetramethyl succinonitrile.

Samples of tetramethyl succinonitrile in air were generated using the two-piece vapor generator which is described in Reference No. 1. Solid tetramethyl succinonitrile was placed in the two-piece generator and heated to 55°C in a thermostatically controlled oil bath. Nitrogen was forced through the warm solid at 764 ml/min. The tetramethyl succinonitrile vapor-nitrogen gas mixture was diluted with air at a flow rate of 100 liters/min. These generation conditions gave concentration levels of tetramethyl succinonitrile vapors which were lower than the three desired levels. A second generation was attempted by lowering the dilution air flow rate to 67 liters/min. This generation gave concentrations at each level which were above the three desired levels. The samples were collected for 60 minutes at a rate of approximately 0.9 liter/minute.

Several attempts were made to use an automated syringe drive system (Model 950 Harvard Infusion/Withdrawal Pump) as an absolute generator calibration. Tetramethyl succinonitrile was dissolved in several low boiling hydrocarbons such as acetone and acetone/hexane mixture. Since the concentration of tetramethyl succinonitrile is known in these solutions, the syringe drive system can be used as an absolute generator calibration. However, severe leakage of the tetramethyl succinonitrile solutions past the syringe barrel precluded use of the Harvard syringe drive unit as an absolute generator calibration.

In lieu of the amount of the time spent on the two generation experiments and other generation experiment attempts, further attempts at generating tetramethyl succinonitrile were not made. The data for the second generation experiment were used in the statistical analysis. The data for the first generation experiment are given below. These data are presented for information only and were not used in the statistical evaluation of the method.

Found			
mg	Corr mg*	Liters	mg/cu m
0.0352	0.0513	50.9	1.008
0.0314	0.0482	48.0	1.004
0.0357	0.0517	50.9	1.016
0.0327	0.0492	49.6	0.992
0.0351	0.0512	52.0	0.985
0.0352	0.0513	52.3	0.981
		n = 6	
		mean	0.998
		std dev	0.014
		CV_2	0.014
0.0707	0.0866	51.9	1.669
0.0673	0.0830	49.4	1.680
0.0713	0.0873	49.7	1.756
0.0712	0.0871	48.1	1.811
0.0691	0.0849	49.4	1.719
0.0683	0.0840	51.0	1.647
		n = 6	
		mean	1.714
		std dev	0.061
		CV_2	0.036
0.140	0.167	50.3	3.32
0.142	0.169	50.1	3.37
0.163	0.194	50.5	3.84
0.155	0.185	49.6	3.73
0.154	0.184	51.2	3.59
0.164	0.195	49.9	3.91
		n = 6	
		mean	3.63
		std dev	0.24
		CV_2	0.066

*The equation D.E. = 0.839 - $e^{-53.3 \text{ X mg found}}$ was used to calculate corr mg.

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted with an analyte concentration of 3.63 mg/cu m. The sensitivity of the total hydrocarbon analyzer was not sufficient to determine when a concentration level of 0.182 mg/cu m (5% of the 2X level) would be in the effluent of the front section of the charcoal tube. Therefore, both sections of the charcoal tube (100 mg of charcoal in the front section and 50 mg in the backup section) were used in the breakthrough experiment. Sampling was done at 0.9 liter per minute for 240 minutes. At that time the backup sections of the charcoal tubes were analyzed for tetramethyl succinonitrile. No tetramethyl succinonitrile was found in the backup sections of the charcoal tubes at a detection limit of 0.03 mg/cu m.

Storage Stability

To assess the stability of tetramethyl succinonitrile on charcoal Lot 105, a time study was conducted at the 1X OSHA level. Six tubes containing 100 mg of charcoal Lot 105 were spiked with 4 µl of a 20% (V/V) acetone-hexane solution of tetramethyl succinonitrile containing 34.75 mg/ml. The spiked samples were stored for seven days before analysis. The results of the time study were compared with the 1X D.E.'s in the Analysis Table which represents spiked samples which were analyzed immediately. The time study results are presented below:

mg taken	mg found	D.E.
0.1390	0.1129	0.812
0.1390	0.1168	0.840
0.1390	0.1225	0.881
0.1390	0.1076	0.774
0.1390	0.1108	0.797
0.1390	0.1139	0.819
	mean	0.820
	std dev	0.037
	CV	0.045

From the above results, tetramethyl succinonitrile is stable on charcoal Lot 105 for at least one week.

Discussion

The modification to P&CAM 127 using a 20% V/V acetone-hexane solution was necessary because of the low solubility of tetramethyl succinonitrile in non-polar solvents such as hexane. It was necessary to dissolve 374.5 mg of tetramethyl succinonitrile in 10 ml of a solvent to spike 100-mg portions of charcoal Lot 105 with 2, 4, and 8 µl of a stock standard of tetramethyl succinonitrile (these amounts correspond to the amounts of tetramethyl succinonitrile collected in a 50-liter

sample at 0.5X, 1X and 2X the OSHA standard). This amount of tetramethyl succinonitrile was not soluble in hexane, however, the analyte was soluble in a 20% V/V acetone-hexane solution.

The solubility problem of tetramethyl succinonitrile also limited the sample size to 50 liters. A 100-liter sample would require almost 700 mg of tetramethyl succinonitrile to be dissolved in 10 ml of solvent for preparation of a stock standard. Acetone was the only solvent found which did not interfere in the analysis and in which tetramethyl succinonitrile had a high solubility.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.034$ $\overline{CV}_2 = 0.054$ $\overline{CV}_T = 0.075$

Data Sheet: Tetramethyl Succinonitrile S155

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.0696	0.0565	0.812	0.139	0.119	0.856	0.278	0.248	0.892
0.0696	0.0549	0.789	0.139	0.116	0.835	0.278	0.236	0.849
0.0696	0.0552	0.793	0.139	0.106	0.763	0.278	0.239	0.860
0.0696	0.0570	0.819	0.139	0.115	0.827	0.278	0.232	0.835
0.0696	0.0537	0.772	0.139	0.115	0.827	0.278	0.229	0.824
0.0696	0.0518	0.744	0.139	0.111	0.799	0.278	0.236	0.849
n =		6			6			6
mean		0.788			0.818			0.852
std dev		0.027			0.032			0.023
CV_1		0.034			0.039			0.027

$\overline{CV}_1$ 0.034

$\overline{CV}_{A+\overline{DE}}$ 0.037

The equation D.E. = $0.839 - e^{-53.3 \times \text{mg found}}$ was used to calculate mg found in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 3.

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Data Sheet: Tetramethyl Succinonitrile S155

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.6S	0.0840	0.1015	56.6	1.793
	0.0833	0.1007	53.3	1.889
	0.0880	0.1060	56.6	1.873
	0.0763	0.0928	55.1	1.684
	0.0825	0.0998	57.8	1.727
	0.0890	0.1072	58.3	1.839
			n = 6	
			mean	1.801
			std dev	0.082
			CV_2	0.046
1.4S	0.210	0.250	57.7	4.33
	0.195	0.232	54.9	4.23
	0.194	0.231	55.2	4.18
	0.183	0.218	53.5	4.07
	0.190	0.226	54.9	4.12
	0.184	0.219	56.7	3.86
			n = 6	
			mean	4.13
			std dev	0.16
			CV_2	0.039
2.7S	0.355	0.423	55.9	7.57
	0.398	0.474	56.1	8.45
	0.414	0.493	55.1	8.95
	0.404	0.482	56.9	8.47
	0.352	0.420	55.4	7.58
	Sample was lost.			
			n = 5	
			mean	8.20
			std dev	0.61
$\overline{CV}_2$ 0.054			CV_2	0.074

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Acrylonitrile, No. S156
OSHA Standard:	20 ppm (45 mg/cu m) - skin
Chemical Used for Validation:	Acrylonitrile Aldrich Chemical

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of acrylonitrile in air is described in NIOSH Method S156, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA standard by spiking 100 mg portions of charcoal Lot 105 with the appropriate amounts of acrylonitrile to represent 20-liter air samples. Samples of acrylonitrile in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with methanol and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of acrylonitrile in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 100 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

Two major modifications were made to P&CAM 127. A hexane solution of acrylonitrile (0.239 g/ml) was used to apply the analyte to the charcoal, so it would not be necessary to inject less than 2 microliters at the 0.5X level. The analyte was desorbed with methanol. The reason for the modification is given in the Discussion Section of this report.

Generation

Samples of acrylonitrile were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-in long stainless steel needle was attached to the syringe. The needle passed through a rubber septum with the end in a heated glass tube. The syringe drive pump delivered 2.85 mg/min of acrylonitrile into the tube. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.6 liters/min

and it was diluted with air at a rate of 33.0 liters/min immediately downstream from the heated zone to obtain the 2X OSHA level. The 2X chamber was monitored with the hydrocarbon analyzer during sampling. Additional dilutions were made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1.

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using the rate of delivery of the syringe drive and the flow rates of the dilution air. These concentrations were also confirmed by comparison with the response of the total hydrocarbon analyzer.

Samples were collected for 100.0 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test. Less than 5% of the generated concentration of 92.0 mg/cu m was present in the effluent after four hours of sampling at a rate of 0.20 liter per minute at which time the test was discontinued. Breakthrough was not observed.

Discussion

Preliminary work on acrylonitrile was conducted at the 1X OSHA standard level to find a suitable desorbing solvent. A hydrogen flame ionization gas chromatographic method was used in this study. The GC conditions are given below:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 235°C injector temperature
5. 255°C detector temperature
6. 155°C column temperature

A stainless steel column (4-ft x 1/4-in) packed with 50/80 mesh Porapak Type Q was used.

Carbon disulfide, 95% ethanol, acetone, methylene chloride, isopropyl alcohol, ethyl acetate, and methanol were tested as possible desorbing solvents. Carbon disulfide and ethyl acetate peaks interfere with the acrylonitrile peak on the gas chromaotgram. There are impurities in the carbon disulfide which interfere with acrylonitrile at this low level. Acetone, 95% ethanol, and methylene chloride elute too close to acrylonitrile. Isopropyl alcohol elutes at the same time as acrylonitrile. Methanol was found to elute before acrylonitrile with good separation. For this reason, methanol was chosen as the desorbing solvent.

A time study was conducted to determine the recovery of acrylonitrile on charcoal, Lot 105, when added from a vapor phase. Six samples at each of the three levels were generated using the syringe drive pump as described under the Generation Section. Three of the samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the charcoal tubes. The samples were allowed to stand for one week before analysis. The samples were desorbed with methanol. The results given below support the conclusion that samples are stable for at least one week in the presence of air. These results were compared with the data in the Sampling and Analysis Table which are the results of the generated samples which were analyzed immediately.

TIME STUDY OF ACRYLONITRILE

	Found				Taken	
	mg	corr mg	Liter	mg/cu m	mg/cu m	Recovery
			FLUSHED WITH NITROGEN			
0.5X	0.313	0.392	21.45	18.28	17.5	
	0.298	0.377	20.49	18.40	17.5	
	Sample was lost.					
			mean	18.34		104.8
1X	0.566	0.666	18.57	35.9	35.0	
	0.565	0.665	18.46	36.0	35.0	
	0.546	0.643	17.82	36.1	35.0	
			mean	36.0		102.9
2X	1.047	1.223	17.93	68.2	70.0	
	1.193	1.394	19.95	69.9	70.0	
	1.189	1.389	19.63	70.8	70.0	
			mean	69.6		99.4

TIME STUDY OF ACRYLONITRILE Continued

	mg	corr mg	Liter	mg/cu m	mg/cu m	Recovery
			NOT FLUSHED WITH NITROGEN			
0.5X	0.299	0.378	20.49	18.45	17.5	
	0.325	0.404	22.09	18.29	17.5	
	0.308	0.387	21.23	18.23	17.5	
			mean	18.32		104.7
1X	0.500	0.591	16.43	36.0	35.0	
	0.557	0.655	18.25	35.9	35.0	
	0.556	0.654	18.89	34.6	35.0	
			mean	35.5		101.4
2X	1.190	1.390	19.85	70.0	70.0	
	1.178	1.376	19.21	71.6	70.0	
	1.138	1.329	18.89	70.4	70.0	
			mean	70.7		101.0

The equation on page S156-5 was used to calculate the corr mg.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis were applied to the data for acrylonitrile as in Reference No. 3. The CV_2 values at the 0.5X, 1X, and 2X levels ranged from 1% to 8%, giving a chi squared value of 14.5. Consequently the CV_2's did not pass the Bartlett's test. However, the results are considered to be satisfactory. For this reason, $\overline{CV}_T$ was calculated on all the data. The statistical procedures used are described in Reference No. 4.

$$\overline{CV}_1 = 0.021 \qquad \overline{CV}_2 = 0.052 \qquad \overline{CV}_T = 0.073$$

The average recovery at the OSHA standard level was 94.0%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

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Data Sheet: Acrylonitrile S156

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.478	0.382	0.799	0.956	0.806	0.843	1.913	1.679	0.878
0.478	0.390	0.816	0.956	0.811	0.848	1.913	1.666	0.871
0.478	0.389	0.814	0.956	0.810	0.847	1.913	1.666	0.871
0.478	0.416	0.870	0.956	0.819	0.857	1.913	1.656	0.866
0.478	0.409	0.856	0.956	0.796	0.833	1.913	1.660	0.868
0.478	0.402	0.841	0.956	0.780	0.816	1.913	1.644	0.859
n =		6			6			6
mean		0.833			0.841			0.869
std dev		0.027			0.014			0.006
CV_1		0.032			0.017			0.007

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{DE}}$ 0.023

The equation D.E. = $0.856 - e^{-9.16 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 5.

Data Sheet: Acrylonitrile S156

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.258	0.339	19.20	17.66	17.50	
	0.286	0.365	20.10	18.16	17.50	
	0.281	0.360	20.70	17.39	17.50	
	0.267	0.347	19.90	17.44	17.50	
	0.263	0.343	19.20	17.87	17.50	
	0.231	0.314	18.80	16.70	17.50	
			n = 6			
			mean	17.54		100.2
			std dev	0.50		
			CV_2	0.028		
1S	0.475	0.563	17.40	32.4	35.0	
	0.486	0.576	17.30	33.3	35.0	
	0.431	0.515	15.40	33.4	35.0	
	0.461	0.548	16.70	32.8	35.0	
	0.469	0.557	17.10	32.6	35.0	
	0.491	0.581	17.70	32.8	35.0	
			n = 6			
			mean	32.9		94.0
			std dev	0.4		
			CV_2	0.012		
2S	0.882	1.030	16.80	61.3	70.0	
	1.086	1.269	18.70	67.9	70.0	
	1.037	1.211	18.60	65.1	70.0	
	0.984	1.150	18.40	62.5	70.0	
	1.163	1.359	18.00	75.5	70.0	
	0.924	1.079	17.70	61.0	70.0	
			n = 6			
			mean	65.6		93.7
			std dev	5.5		
$\overline{CV}_2$ 0.052			CV_2	0.084		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Phenylhydrazine, No. S160
OSHA Standard:	5 ppm (22 mg/cu m) -- skin
Chemicals Used for Validation:	Phenylhydrazine and Phenylhydrazine Hydrochloride J. T. Baker Chemical Company

Procedure

The procedure validated for collecting and analyzing phenylhydrazine in air is described in NIOSH Method S160. The analysis is based upon the colorimetric molybdenum blue method described in Reference No. 1. Standard samples were prepared and a standard curve was constructed by plotting absorbance versus equivalent mg of phenylhydrazine. Samples of phenylhydrazine were generated as described below and collected in standard midget bubblers (impingers fitted with fritted glass tipped inlet tubes) containing 15 ml of 0.1 N hydrochloric acid. Collection efficiency tests were done at 2X the OSHA standard level. The found mg of phenylhydrazine in the generated samples were determined by reading the mg found from the standard curve. The concentrations of phenylhydrazine in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 100 minutes).

Modification of Reference 1

After addition of the phosphomolybdic acid reagent, the samples were not heated as described in Reference 1. It was found experimentally that the color reaction with phenylhydrazine is very rapid at room temperature, and heating the samples at 75°C for 1 hour produced no change in the absorbance of the test samples. The intensity of the developed color was determined at 730 nm using a Cary Model 14M spectrophotometer with either an IR source or a tungsten lamp; both sources gave identical absorbance readings at 730 nm. Larger dilutions were employed to accommodate the collection method; however, the high sensitivity of the analytical method allowed accuracy to be maintained. Phenylhydrazine hydrochloride was used as the standard for the calibration curve.

Analysis

Phenylhydrazine is slowly air-oxidized and is difficult to maintain in known purity. The validation of the analytical method was therefore done using phenylhydrazine hydrochloride. The standard calibration curve prepared with this salt as received, was identical to that obtained with a sample recrystallized from hot absolute ethanol. The standards should be prepared in dilute HCl, because standards prepared in water are unstable and must be prepared fresh daily. A time study indicated that the collected samples in dilute hydrochloric acid could be stored covered at room temperature as long as five days

before analysis with no loss in absorbance reading. The analyte for spiking was obtained from a newly opened bottle of phenylhydrazine. The time study results are given below:

TIME STUDY OF PHENYLHYDRAZINE AFTER FIVE DAYS

mg added	mg found after 5 days	% Recovery
4.4	4.4	100
4.4	4.5	102
4.4	4.4	100
4.4	4.3	98
4.4	4.4	100
4.4	4.4	100

Purity of the commercial phenylhydrazine was checked periodically on a gas chromatograph using the following conditions: Carbowax 20M column; column temperature 130°C; injector and detector temperature 220°C.

Two major impurities were found which eluted from the column before phenylhydrazine, and a minor one which appeared shortly after the analyte. The samples were therefore purified by basifying the phenylhydrazine hydrochloride and extracting with dichloromethane. The purified samples were injected into the gas chromatograph, using an alternate column (Chromosorb 103) and a lower injection temperature, and the impurity still remained. It was concluded that phenylhydrazine was not necessarily impure, but could have been decomposing on the column. An independent analytical method of establishing the phenylhydrazine concentration in the generation procedure was therefore not used.

Generation

The basic procedure used to generate phenylhydrazine was to use a calibrated syringe drive for delivery of the sample into an enclosed heated glass tube. The sample was delivered at a rate of 2.093 mg/min. Nitrogen at a flow rate of 21.3 liters per minute was passed over the sample in the heated zone in order to minimize oxidation during vaporization of the analyte. The tube was packed with glass wool for more complete mixing and uniform dilution. Just beyond the heated zone, air at a flow rate of 15.1 liters per minute at 23°C diluted the sample vapor to obtain the 2X OSHA level concentration. The actual concentrations at the 2X level could not be accurately determined from the syringe drive rate because of condensation of some analyte on the walls of the apparatus. Rinsing of the walls of the generation apparatus with acetone produced a yellow solution, indicating the presence of phenylhydrazine. Known dilutions were made to obtain the 1X and 0.5X OSHA standard levels. The dilution system is described in Reference No. 2. Six samples at each of the three levels were collected simultaneously at 1 liter per minute for a sampling time of 100 minutes.

Collection Efficiency

The collection efficiency was determined by connecting a pair of bubblers in series at each of the six sampling ports at the 2X OSHA level, and collecting at a concentration of 44.8 mg/cu m at a rate of 1 liter per minute for 100 minutes. Each bubbler was analyzed separately and compared to a standard calibration curve. No phenylhydrazine was detected in the second backup bubbler. The collection efficiency of the bubblers was considered to be 1.00 ± 0.01. Therefore, the found concentrations were assumed to be an accurate measure of the concentrations in the generator.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.023$ $\overline{CV}_2 = 0.032$ $\overline{CV}_T = 0.060$

Data Sheet: Phenylhydrazine S160

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	Recovery (%)	mg taken	mg found	Recovery (%)	mg taken	mg found	Recovery (%)
1.099	1.07	97.4	2.197	2.05	93.3	4.39	4.19	95.4
1.099	1.12	101.9	2.197	2.01	91.5	4.39	4.15	94.5
1.099	1.10	100.1	2.197	1.95	88.8	4.39	4.13	94.1
1.099	1.12	101.9	2.197	2.05	93.3	4.39	3.87	88.2
1.099	1.12	101.9	2.197	1.99	90.6	4.39	4.07	92.7
1.099	1.12	101.9	2.197	2.01	91.5	4.39	4.17	95.0
n =		6			6			6
mean		100.9			91.5			93.3
std dev		1.8			1.7			2.7
CV_1		0.018			0.019			0.029

$\overline{CV}_1$ 0.023

$\overline{CV}_{A+\overline{DE}}$ 0.025

Data Sheet: Phenylhydrazine S160

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.86	84.5	10.18
	0.98	91.3	10.73
	0.94	90.2	10.42
	0.97	93.0	10.43
	0.97	90.9	10.67
	0.95	96.7	9.82
		n = 6	
		mean	10.38
		std dev	0.34
		CV_2	0.033
1S	1.82	80.0	22.75
	1.92	87.6	21.92
	1.83	87.6	20.89
	1.83	86.3	21.21
	2.10	92.7	22.65
	1.74	81.4	21.38
		n = 6	
		mean	21.80
		std dev	0.77
		CV_2	0.035
2S	3.89	84.2	46.2
	4.01	88.2	45.5
	4.05	93.0	43.5
	3.89	87.2	44.6
	3.99	90.2	44.2
	Sample lost due to malfunctioning orifice.		
		n = 5	
		mean	44.8
		std dev	1.1
$\overline{CV}_2$ 0.032		CV_2	0.025

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. L. Feinsilver, J. A. Perregrino, and C. J. Smith, Jr., "Estimation of Hydrazine and Three of Its Methyl Derivatives," Industrial Hygiene Journal, 20, February 1959, 26-31.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Pyridine, No. S161
OSHA Standard:	5 ppm (15 mg/cu m)
Chemical used for validation:	Pyridine J. T. Baker

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of pyridine in air is described in NIOSH Method S161, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid pyridine to represent 100-liter air samples. Samples of pyridine in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with methylene chloride and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of pyridine in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 108.3 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined from the delivery rate of a syringe drive pump and the flow rates of the dilution air and were confirmed with bag standards and a total hydrocarbon analyzer.

Modifications

Two major modifications were made to P&CAM 127. A hexane solution of pyridine (393 mg/ml) was used to apply the analyte to the charcoal, so it would not be necessary to inject less than 2 microliters at the 0.5X level. The analyte was desorbed with methylene chloride. The reason for the modification is given in the Discussion Section of this report.

Generation

Samples of pyridine were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-in long stainless steel needle was attached to the syringe. The other end of the needle passed through a rubber septum into a heated glass tube maintained at 200°C. The syringe drive pump delivered 3.22 mg/min of pyridine into the tube. The tube was packed with glass beads to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 3.60 liters/minute and diluted with air at a rate of 22.33 liters/minute immediately after the heated zone. This concentration was

monitored by a total hydrocarbon analyzer and compared to bag standards at 126 mg/cu m. Further dilution with air at a rate of 80.01 liters/minute was made to obtain the 2X OSHA level. The 2X chamber was monitored with the hydrocarbon analyzer during sampling. Dilutions were again made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1.

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using the rate of delivery of the syringe drive and the flow rates of the dilution air. These concentrations were also confirmed by comparison with bag standards.

Samples were collected for 108.3 minutes at a rate of approximately 1.0 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. A total hydrocarbon analyzer was used. Less than 5% of the generated concentration of 30.4 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 1 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

Preliminary desorption efficiency trials were conducted at 1X the OSHA standard level. The GC conditions used are given below:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 260°C injector temperature
5. 285°C manifold temperature (detector)
6. 140°C column temperature

A stainless steel column (10-ft X 1/8-in) packed with 5% Carbowax 20M on 80/100 mesh acid washed DMCS Chromosorb W was used.

Carbon disulfide, methanol, and methylene chloride were tested as possible desorbing solvents. Carbon disulfide gave an average D.E. of 0.734; methanol gave a D.E. of 0.201. Methylene chloride was chosen because it gave a D.E. of 0.817. The D.E. results are given in the Analysis Data Sheet at the end of this report.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.013$ $\overline{CV}_2 = 0.030$ $\overline{CV}_T = 0.059$

The average recovery at the OSHA standard level was 106.3%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Pyridine, S161

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.786	0.626	0.796	1.571	1.284	0.817	3.14	2.55	0.812
0.786	0.622	0.791	1.571	1.286	0.819	3.14	2.50	0.796
0.786	0.638	0.812	1.571	1.283	0.817	3.14	2.52	0.803
0.786	0.628	0.799	1.571	1.278	0.813	3.14	2.60	0.828
0.786	0.626	0.796	1.571	1.286	0.819	3.14	2.62	0.834
0.786	0.620	0.789	1.571	1.286	0.819	3.14	2.61	0.831
n =		6			6			6
mean		0.797			0.817			0.817
std dev		0.008			0.002			0.016
CV_1		0.010			0.002			0.020

$\overline{CV}_1$ 0.013

$\overline{CV}_{A+\overline{DE}}$ 0.014

The equation D.E. = $0.818 - e^{-6.20 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Pyridine , S161

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.704	0.875	102.1	8.57	7.59	
	0.665	0.830	105.2	7.89	7.59	
	0.654	0.816	96.2	8.48	7.59	
	0.661	0.825	99.4	8.30	7.59	
	0.662	0.825	101.7	8.11	7.59	
	0.705	0.876	104.4	8.39	7.59	
			n = 6			
			mean	8.29		109.2
			std dev	0.25		
			CV_2	0.030		
1S	1.360	1.663	96.7	17.20	15.19	
	1.387	1.696	104.8	16.18	15.19	
	1.316	1.609	104.2	15.44	15.19	
	1.294	1.582	99.1	15.96	15.19	
	1.284	1.570	99.6	15.76	15.19	
	1.325	1.620	99.1	16.35	15.19	
			n = 6			
			mean	16.15		106.3
			std dev	0.61		
			CV_2	0.038		
2S	2.877	3.52	101.9	34.5	30.4	
	2.882	3.52	101.3	34.7	30.4	
	2.760	3.37	100.6	33.5	30.4	
	2.740	3.35	99.4	33.7	30.4	
	2.930	3.58	102.8	34.8	30.4	
	2.751	3.36	100.9	33.3	30.4	
			n = 6			
			mean	34.1		112.2
			std dev	0.7		
$\overline{CV}_2$ 0.030			CV_2	0.021		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Xylidine (2,4-Dimethylaminobenzene), No. S162
OSHA Standard:	5 ppm (25 mg/cu m) - skin
Chemical used for Validation:	Xylidine (2,4-Dimethylaminobenzene) J. T. Baker Chemical Company

Procedure

The procedure for collecting and analyzing concentrations of xylidine in air is described in NIOSH Method S162, which has been adapted from P&CAM 168. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of xylidine to represent 20-liter air samples. Samples of xylidine were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with 95% ethanol in an ultrasonic bath for one hour and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for D.E. to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 110 minutes). The "true" concentration at the 2X, 1X, and 0.5X OSHA standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were three major modifications made to P&CAM 168. The analyte was collected in 7-cm long by 4-mm I.D. silica gel tubes containing 150 mg of 20/40 mesh silica gel in the adsorbing section and 75 mg in the backup section instead of the 12.5-cm long by 8-mm I.D. tubes containing 700 mg of 45/60 mesh silica gel in the adsorbing section and 150 mg in the backup section. A hexane solution of xylidine (125 mg/ml) was used to apply the analyte to the silica gel, so it would not be necessary to inject less than 2 µl at the 0.5X level. Desorption was done for one hour in an ultrasonic bath to aid the desorption process.

Generation

Samples of xylidine were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950).

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* Silica gel tubes were obtained from Environmental Compliance Corp.

A 2-ml syringe was filled with xylidine and placed in the syringe drive pump. The syringe fitted with a 15-inch long stainless steel needle delivered the analyte into a heated glass tube at a rate of 1.94 mg/minute. The tube was packed with glass beads to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.59 liters/minute and diluted with air at a rate of 31.2 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

Samples were collected for 110 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 50.0 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.20 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

The 7-cm silica gel tubes packed with 20/40 mesh silica gel were used instead of the larger 12.5-cm tubes packed with 45/60 mesh silica gel recommended in P&CAM 168, because the pressure drop across the larger tubes, which were tightly packed with a finer mesh size of silica gel, was too great at a flow rate of 1 liter per minute.

A time study at the 1X OSHA level was conducted to test the stability of xylidine on silica gel. Six tubes were spiked using a hexane solution of xylidine and allowed to stand at room temperature for a period of one week before analysis. The samples were desorbed with 95% ethanol for one hour in an ultrasonic bath. The results are given below:

mg taken	mg found	D.E.
0.505	0.430	0.851
0.505	0.430	0.851
0.505	0.433	0.857
0.505	0.441	0.873
0.505	0.449	0.889
	mean	0.864

The above recoveries were compared with the 1X level D.E.'s from samples which were analyzed after standing at room temperature for one day. The average recovery for these samples was 0.979. Because of the difference in the two sets of recoveries, a second time study was conducted. The purpose of the second time study was to test the recovery behavior of xylidine on silica gel when added from a vapor phase versus addition from a hexane solution as described above. Six samples at 2X the OSHA standard level were generated using the syringe drive pump as described under the Generation Section. Three samples were analyzed on the same day they were generated and the remaining three samples were allowed to stand for one week before analysis. The samples were desorbed with 95% ethanol for one hour in an ultrasonic bath. The results are given below:

TIME STUDY RESULTS OF XYLIDINE
(ANALYZED SAME DAY AS THE GENERATION)

Found				Taken	
mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
0.964	0.965	20.35	47.4	50.0	
0.936	0.937	20.35	46.0	50.0	
0.900	0.901	19.47	46.3	50.0	
		mean	46.6		93.2

TIME STUDY RESULTS OF XYLIDINE
(ANALYZED AFTER 1 WEEK OF STORAGE)

Found				Taken	
mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
0.940	0.941	20.68	45.5	50.0	
0.894	0.895	20.35	44.0	50.0	
0.956	0.957	20.02	47.8	50.0	
		mean	45.8		91.6

From the above results, xylidine is stable for at least one week on silica gel. A third time study was conducted by generating five samples at 2X the OSHA standard. Two of the samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the silica gel tubes. The samples were allowed to stand for one week before analysis. The samples were desorbed with 95% ethanol for 1 hour in an ultrasonic bath. The results are given on the next page.

TIME STUDY RESULTS OF XYLIDINE
(FLUSHED WITH NITROGEN)

Found				Taken	
mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
0.942	0.943	20.35	46.3	50.0	
0.947	0.948	20.35	46.6	50.0	
		mean	46.4		92.8
			(CAPPED)		
1.035	1.036	20.68	50.1	50.0	
0.960	0.961	20.35	47.2	50.0	
0.926	0.927	20.02	46.3	50.0	
		mean	47.9		95.8

Based on the three studies described above, it was concluded that xylidine is adequately stable on silica gel for at least one week without flushing the tubes with nitrogen.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.021$ $\overline{CV}_2 = 0.026$ $\overline{CV}_T = 0.057$

The average recovery at the OSHA standard level was 105.4%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Xylidine S162

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.2527	0.2426	0.960	0.505	0.493	0.976	1.011	0.999	0.988
0.2527	0.2398	0.949	0.505	0.484	0.958	1.011	1.013	1.002
0.2527	0.2430	0.962	0.505	0.481	0.952	1.011	1.039	1.028
0.2527	0.2491	0.986	0.505	0.495	0.980	1.011	1.057	1.046
0.2527	0.2443	0.967	0.505	0.509	1.008	1.011	1.021	1.010
0.2527	0.2350	0.930	0.505	0.505	1.000	1.011	1.026	1.015
n =		6			6			6
mean		0.959			0.979			1.015
std dev		0.019			0.022			0.020
CV_1		0.020			0.022			0.020

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{DE}}$ 0.023

The equation D.E. = $0.999 - e^{-13.10 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Xylidine S162

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.2426	0.2535	21.01	12.07	12.51	
	0.2522	0.2622	22.11	11.86	12.51	
	0.2597	0.2688	22.88	11.75	12.51	
	0.2528	0.2625	21.78	12.05	12.51	
	0.2406	0.2517	21.12	11.92	12.51	
	0.2344	0.2460	20.68	11.90	12.51	
			n = 6			
			mean	11.92		95.3
			std dev	0.12		
			CV_2	0.010		
1S	0.498	0.499	19.25	25.92	25.02	
	0.499	0.500	19.25	25.97	25.02	
	0.449	0.451	16.94	26.62	25.02	
	0.492	0.493	18.26	27.00	25.02	
	0.477	0.478	18.04	26.50	25.02	
	0.488	0.489	18.59	26.30	25.02	
			n = 6			
			mean	26.38		105.4
			std dev	0.41		
			CV_2	0.016		
2S	0.940	0.941	20.68	45.5	50.0	
	0.924	0.925	20.35	45.5	50.0	
	1.005	1.006	20.35	49.4	50.0	
	0.975	0.976	20.35	48.0	50.0	
	0.980	0.981	20.02	49.0	50.0	
	0.961	0.962	19.47	49.4	50.0	
			n = 6			
			mean	47.8		95.6
			std dev	1.9		
$\overline{CV}_2$ 0.026			CV_2	0.040		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Dimethylaniline, No. S164
OSHA Standard:	5 ppm (25 mg/cu m)
Chemical used for validation:	Dimethylaniline Lot 9219 J. T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of dimethylaniline in air is described in NIOSH Method S164, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100-mg portions of charcoal with the appropriate amounts of liquid dimethylaniline to represent 20-liter air samples. Samples of dimethylaniline in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.), and the "found" concentrations of dimethylaniline in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample x 105 minutes). The "true" concentrations of dimethylaniline in the generated samples were determined by comparison with a "bag" standard using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There was one major modification to P&CAM 127.

A hexane solution containing 312.5 mg/ml of dimethylaniline was used to apply the analyte to the charcoal. This was done so it would not be necessary to inject less than 2 microliters at the 0.5X level.

Generation

Samples of dimethylaniline in air were generated by the procedure described in the Backup Data Report for Epichlorohydrin (Reference No. 2). The generator conditions used are given in the following table:

Generator Conditions
for
Dimethylaniline

Nitrogen flow rate	0.370 liter/minute at 22°C
Dilution air flow rate	28.0 liters/minute at 22°C
Bath temperature	25°C

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations at the three concentration levels (Reference No. 1). Samples were collected for 105 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 1). Less than 5% of the generated concentration of 47 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.186 liter per minute, indicating a capacity of at least 2.1 mg of dimethylaniline in the charcoal tube.

Discussion

A time study was conducted at 1X the OSHA standard level to test the stability of dimethylaniline on charcoal Lot 105. Two sets of six tubes (each containing 100 mg of charcoal Lot 105) were spiked three days apart and analyzed on the same day. There was no significant difference in the recoveries of the two sets of tubes.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for dimethylaniline as in Reference No. 4.

The sampling and analysis data gave a chi squared value of 20.1 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. Therefore, CV_T is calculated only on the data at the 1X level.

$$CV_T = \sqrt{CV_2^2 + (0.05)^2} = 0.052$$

where:

CV_2 = Coefficient of Variation at the 1X level for Sampling and Analysis = 0.013

(0.05) = pump error

The average recovery at the OSHA standard level was 91.4%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, CV_T is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Dimethylaniline S164

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.2486	0.2116	0.851	0.497	0.436	0.877	0.994	0.862	0.867
0.2486	0.2102	0.846	0.497	0.444	0.893	0.994	0.853	0.858
0.2486	0.2046	0.823	0.497	0.435	0.875	0.994	0.861	0.866
0.2486	0.2122	0.854	0.497	0.427	0.859	0.994	0.858	0.863
0.2486	0.2071	0.833	0.497	0.426	0.857	0.994	0.855	0.860
0.2486	0.2174	0.874	0.497	0.440	0.885	0.994	0.849	0.854
n =		6			6			6
mean		0.847			0.874			0.861
std dev		0.018			0.014			0.005
CV_1		0.021			0.016			0.006

The equation D.E. = $0.868 - e^{-18.12 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 5.

Data Sheet: Dimethylaniline S164

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.177	0.214	21.84	9.80	10.48	
	0.169	0.206	21.11	9.76	10.48	
	0.167	0.204	20.79	9.81	10.48	
	0.156	0.193	20.06	9.62	10.48	
	0.157	0.194	19.74	9.83	10.48	
	0.154	0.191	20.16	9.47	10.48	
			n = 6			
			mean	9.72		92.7
			std dev	0.14		
			CV_2	0.014		
1S	0.267	0.310	16.17	19.17	20.74	
	0.281	0.326	17.43	18.70	20.74	
	0.280	0.325	17.22	18.87	20.74	
	0.304	0.352	18.38	19.15	20.74	
	0.294	0.341	17.75	19.21	20.74	
	0.283	0.343	18.38	18.66	20.74	
			n = 6			
			mean	18.96		91.4
			std dev	0.25		
			CV_2	0.013		
2S	0.679	0.782	18.59	42.1	46.7	
	0.838	0.965	19.74	48.9	46.7	
	0.820	0.945	19.11	49.5	46.7	
	0.799	0.921	19.43	47.4	46.7	
	0.671	0.773	19.43	39.8	46.7	
	Sample lost due to malfunctioning orifice.					
			n = 5			
			mean	45.5		97.4
			std dev	4.3		
			CV_2	0.094		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

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References

1. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Acetonitrile, No. S165
OSHA Standard:	40 ppm (70 mg/cu m)
Chemical used for validation:	Acetonitrile Mallinkrodt Chemical Co.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of acetonitrile in air is described in NIOSH Method S165, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 400 mg of charcoal with the appropriate amounts of acetonitrile to represent 10-liter air samples. Samples of acetonitrile in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with benzene and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of acetonitrile in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 60 minutes). The "true" concentrations of acetonitrile in the generated samples were determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration.

Modifications

There were four major modifications to P&CAM 127.

A benzene solution of acetonitrile containing 157 mg/ml of acetonitrile was used to apply the analyte to the charcoal, so it would not be necessary to inject less than 2 µl at the 0.5X level. A hexane solution was not used, because acetonitrile is not very soluble in hexane.

Benzene, instead of carbon disulfide, was used as the desorbing solvent for the method. Five milliliters, instead of one milliliter, of the desorbing solvent was used.

Large charcoal tubes from SKC, Inc. (9 mm long with a 8-mm O.D. and 6-mm I.D.) were used to collect acetonitrile instead of the smaller charcoal tubes (7 cm long with a 6-mm O.D. and a 4-mm I.D.). (See Discussion Section)

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Generation

Samples of acetonitrile in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 1). The generator conditions used are given in the following table:

Generator Conditions
for
Acetonitrile

Nitrogen flow rate	0.20 liters/minute at 22°C
Dilution air flow rate	81.7 liters/minute at 22°C
Bath temperature	0°C

A Beckman Model 402 total hydrocarbon analyzer was used to monitor the generated vapor concentrations (Reference No. 2). Samples were collected for 60 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the large charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 2). Breakthrough occurred in 190 minutes when a concentration of 140 mg/cu m was sampled at a rate of 0.196 liter per minute.

Discussion

The GC conditions used with a 4-ft X 1/4-in stainless steel column packed with 50/80 mesh Porapak Q were as follows:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 270°C injector temperature
5. 285°C detector temperature
6. 180°C column temperature

It was necessary to choose another desorbing solvent for the method, because carbon disulfide gave a peak that interfered with the acetonitrile peak on the gas chromatogram.

Benzene was tried, and benzene did not interfere on the gas chromatogram. Benzene also gave satisfactory recoveries of acetonitrile. Desorption efficiency tests were conducted for 30 minutes, and the D.E.'s were satisfactory. Therefore, no further work on desorption time dependence was conducted.

Large charcoal tubes from SKC, Inc., containing 400 mg of charcoal Lot 105 in the front section of the tube and 200 mg in the back section, were used to collect the acetonitrile samples. It was necessary to use these large charcoal tubes, because breakthrough occurs in 38 minutes with the smaller charcoal tubes (100 mg of charcoal Lot 105 in the front section of the tube and 50 mg in the backup section). Breakthrough tests were also conducted on small silica gel tubes and breakthrough occurred in 70 minutes. It was therefore decided to use the larger charcoal tubes to obtain a longer sampling time.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.047$ $\overline{CV}_2 = 0.048$ $\overline{CV}_T = 0.072$

The average recovery at the OSHA standard level was 105.3%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Acetonitrile S165

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.346	0.260	0.751	0.692	0.588	0.850	1.383	1.109	0.802
0.346	0.257	0.743	0.692	0.581	0.840	1.383	1.100	0.795
0.346	0.297	0.858	0.692	0.516	0.746	1.383	1.142	0.826
0.346	0.261	0.754	0.692	0.564	0.815	1.383	1.183	0.855
0.346	0.264	0.763	0.692	0.573	0.828	1.383	1.204	0.871
0.346	0.270	0.780	0.692	0.555	0.802	1.383	1.192	0.862
n =		6			6			6
mean		0.775			0.814			0.835
std dev		0.043			0.037			0.032
CV_1		0.055			0.045			0.038

$\overline{CV}_1$ 0.047

$\overline{CV}_{A+\overline{DE}}$ 0.051

The equation D.E. = $0.828 - e^{-10.68 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is documented in Reference No. 4.

Data Sheet: Acetonitrile S165

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.304	0.385	11.88	32.4	31.4	
	0.313	0.395	12.06	32.8	31.4	
	0.297	0.378	11.46	33.0	31.4	
	0.283	0.363	11.28	32.2	31.4	
	0.280	0.360	11.52	31.2	31.4	
	0.334	0.418	12.48	33.5	31.4	
			n = 6			
			mean	32.5		103.5
			std dev	0.8		
			CV_2	0.025		
1S	0.551	0.668	10.50	63.6	62.1	
	0.505	0.614	9.24	66.4	62.1	
	0.542	0.657	9.96	66.0	62.1	
	0.557	0.675	10.50	64.3	62.1	
	0.529	0.642	9.84	65.2	62.1	
	0.561	0.679	10.14	67.0	62.1	
			n = 6			
			mean	65.4		105.3
			std dev	1.3		
			CV_2	0.020		
2S	1.332	1.609	10.92	147.3	140.2	
	1.380	1.667	11.10	150.2	140.2	
	1.484	1.792	10.62	168.7	140.2	
	1.253	1.513	11.10	136.3	140.2	
	1.319	1.593	11.28	141.2	140.2	
	Defective orifice.					
			n = 5			
			mean	148.7		106.1
			std dev	12.4		
$\overline{CV}_2$	0.048		CV_2	0.083		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Cresol (all isomers), No. S167
OSHA Standard:	5 ppm (22 mg/cu m) - skin
Chemicals used for Validation:	o-Cresol, m-Cresol, and p-Cresol J. T. Baker Chemical Company

Procedure

The procedure for collecting and analyzing concentrations of the isomers of cresol in air is described in NIOSH Method S167, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with the appropriate amounts of a mixture containing the isomers of cresol to represent 20-liter air samples. Samples of the isomers of cresol in air were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with acetone and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for D.E. to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 110 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling. The concentrations derived from the syringe drive pump were believed to be more reliable because of difficulty in calibrating the total hydrocarbon analyzer for such a low concentration of analyte.

Modifications

Three major modifications were made to P&CAM 127. A mixture of the three isomers was prepared; a hexane solution of the mixture containing 110 mg/ml was used to apply the analyte onto the silica gel so it would not be necessary to inject less than 2 microliters at the 0.5X level. The samples were collected on silica gel tubes, and the analyte was desorbed with acetone. The reasons for these modifications are discussed in the Discussion Section of this report.

Generation

Samples of the three isomers of cresol were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the mixture of isomers

* Silica gel tubes were obtained from Environmental Compliance Corp., Venetia, Pa., Catalog 226-10.

and placed in the syringe-drive pump. The mixture of the isomers was made by mixing together 20 ml of the ortho-, 40 ml of the meta-, and 30 ml of the para- cresols. A 15-inch long stainless steel needle was attached to the syringe, which delivered the cresols into a heated glass tube at a rate of 2.04 mg/minute. The tube was packed with glass beads to provide a large surface area. The vapor was carried from the first stage of the generator by a stream of nitrogen at 7.78 liters/minute and diluted with air at a rate of 40.62 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

The concentration in the 2X sampling chamber was determined by using the rate of delivery of the syringe drive and the flow rate of the dilution air. Known dilution factors were applied to obtain the 1X and 0.5X OSHA concentrations.

Samples were collected for 110 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 42.2 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.20 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

The GC conditions that were used for the measurement of the cresols were as follows:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 250°C detector temperature
6. 200°C column temperature

A stainless steel column (10-ft x 1/8-in) packed with 10% FFAP on 80/100 mesh acid washed DMCS Chromosorb W was used.

Although there are three isomers of cresol, there are only two peaks on the gas chromatogram, because the meta and para isomers have the same retention time. Preliminary desorption efficiency tests were conducted at 1X the OSHA standard level, using charcoal Lot 105 and 1 ml of carbon disulfide as the desorbing solvent. The average desorption efficiency for 3 tests was 0.015.

Additional desorption efficiency tests were conducted at 1X the OSHA standard level, using charcoal Lot 105 and different desorbing solvents. The results are given in the following table:

DESORPTION EFFICIENCY OF CRESOL (ALL ISOMERS) ON CHARCOAL LOT 105

Solvent (1 ml)	Average Desorption Efficiency
Acetone	0.0159
Methylene Chloride	0.205

Benzene, methanol, and tetrahydrofuran were also tried as possible desorbing solvents, but good reproducible curves from the gas chromatogram could not be obtained.

Because of the poor recoveries of the isomers of cresol from charcoal, silica gel was used to collect the analyte.

Preliminary desorption efficiency trials were conducted on silica gel. The concentrations were measured using the same GC conditions as stated above. Carbon disulfide, methylene chloride, and acetone were tested as possible desorbing solvents. Methylene chloride gave an average D.E. of 0.384, and acetone gave an average D.E. of 1.033. Carbon disulfide gave no measurable recovery of the isomers on silica gel. Based on these results, acetone was chosen. Results, using a 20-liter sample and acetone as the desorbing solvent, are given in the Data Sheets at the end of this report.

A time study at 1X the OSHA standard level was conducted to test the stability of the analyte on silica gel. Six tubes were spiked and allowed to stand for one week before desorption with 1 ml of acetone. The results are given below:

mg taken	mg found	D.E.
0.440	0.497	1.130
0.440	0.491	1.116
0.440	0.496	1.127
0.440	0.410	0.932
0.440	0.420	0.955
0.440	0.416	0.945

From the above results, the analyte is stable on silica gel for at least one week.

During analysis of the generated samples of the analyte on silica gel, it was discovered that the glass wool in front of the adsorbing section of the silica gel tube was yellow for several samples at the 2X level. It is therefore recommended that the glass wool be analyzed along with the sample to avoid sample loss.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.028$ $\overline{CV}_2 = 0.044$ $\overline{CV}_T = 0.068$

The average recovery at the OSHA standard level was 95.8%.

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Cresol (all isomers) S167

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.225	0.223	0.991	0.450	0.448	0.996	0.899	0.933	1.038
0.225	0.222	0.987	0.450	0.452	1.004	0.899	0.930	1.034
0.225	0.212	0.942	0.450	0.465	1.033	0.899	0.869	0.967
0.225	0.228	1.013	0.450	0.483	1.073	0.899	0.900	1.001
0.225	0.223	0.991	0.450	0.472	1.049	0.899	0.879	0.978
0.225	0.215	0.956	0.450	0.469	1.042	0.899	0.924	1.028
n =		6			6			6
mean		0.980			1.033			1.008
std dev		0.026			0.029			0.030
CV_1		0.027			0.028			0.030

$\overline{CV}_1$ 0.028

$\overline{CV}_{A+\overline{DE}}$ 0.030

The equation D.E. = $1.021 - e^{-14.43 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

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Data Sheet: Cresol (all isomers) S167

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.1883	0.1972	20.68	9.54	10.54	
	0.1996	0.2068	22.11	9.35	10.54	
	0.2045	0.2110	21.12	9.99	10.54	
	0.2202	0.2249	22.88	9.83	10.54	
	0.1957	0.2034	21.01	9.68	10.54	
	0.2009	0.2080	21.78	9.55	10.54	
			n = 6			
			mean	9.66		91.7
			std dev	0.23		
			CV_2	0.024		
1S	0.368	0.362	19.25	18.80	21.08	
	0.394	0.387	19.25	20.10	21.08	
	0.353	0.348	18.26	19.06	21.08	
	0.378	0.372	18.04	20.62	21.08	
	0.400	0.393	18.59	21.14	21.08	
	0.369	0.363	16.94	21.43	21.08	
			n = 6			
			mean	20.19		95.8
			std dev	1.08		
			CV_2	0.053		
2S	0.829	0.812	20.02	40.6	42.2	
	0.845	0.828	20.68	40.0	42.2	
	0.855	0.837	20.35	41.1	42.2	
	0.790	0.774	18.59	41.6	42.2	
	0.727	0.712	19.47	36.6	42.2	
	0.784	0.768	20.35	37.7	42.2	
			n = 6			
			mean	39.6		93.8
			std dev	2.0		
$\overline{CV}_2$	0.044		CV_2	0.050		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: o-Toluidine, No. S168

OSHA Standard: 5 ppm (22 mg/cu m) - skin

Chemical used for Validation: o-Toluidine
J. T. Baker Chemical Company

Procedure

The procedure for collecting and analyzing concentrations of o-toluidine in air is described in NIOSH Method S168, which has been adapted from P&CAM 168. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of o-toluidine to represent 50-liter air samples. Samples of o-toluidine were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with 95% ethanol in an ultrasonic bath for one hour and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for D.E. to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 60 minutes). The "true" concentration at the 2X, 1X, and 0.5X OSHA standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were three major modifications made to P&CAM 168. The analyte was collected in 7-cm long by 4-mm I.D. silica gel tubes containing 150 mg of 20/40 mesh silica gel in the adsorbing section and 75 mg in the backup section instead of the 12.5-cm long by 8-mm I.D. tubes containing 700 mg of 45/60 mesh silica gel in the adsorbing section and 150 mg in the backup section. A hexane solution of o-toluidine (0.275 mg/ml) was used to apply the analyte to the silica gel, so it would not be necessary to inject less than 2 µl at the 0.5X level. Desorption was done for one hour in an ultrasonic bath to aid the desorption process.

Generation

Samples of o-toluidine were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950).

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* Silica gel tubes were obtained from Environmental Compliance Corp.

A 2-ml syringe was filled with o-toluidine and placed in the syringe drive pump. The syringe fitted with a 15-inch long stainless steel needle delivered the analyte into a heated glass tube at a rate of 1.98 mg/minute. The tube was packed with glass beads to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.59 liters/minute and diluted with air at a rate of 34.7 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

Samples were collected for 60 minutes at a rate of slightly less than 1.0 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 46.9 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 1.0 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

The 7-cm long silica gel tubes were used instead of the larger 12.5-cm long tubes recommended in P&CAM 168, because the pressure drop across the larger tubes, which were tightly packed with a finer mesh size of silica gel, was too great at a flow rate of 1 liter per minute.

A time study at the 1X OSHA level was conducted to test the stability of o-toluidine on silica gel. Six tubes were spiked using a hexane solution of o-toluidine and allowed to stand for a period of one week before analysis. The samples were desorbed with 95% ethanol for one hour in an ultrasonic bath. The results are given below:

mg taken	mg found	D.E.
2.196	1.961	0.893
2.196	1.637	0.745
2.196	1.586	0.722
2.196	1.843	0.839
2.196	2.003	0.912
2.196	2.335	1.063

Because of the large scatter in the above recoveries, a second time study was conducted. The purpose of the second time study was to determine the recovery of o-toluidine on silica gel when added from

a vapor phase versus addition from a hexane solution as done above. Six samples at each of the three OSHA levels were generated using the syringe drive pump as described under the Generation Section. Three samples at each level were analyzed on the same day of the generation and the remaining three samples were allowed to stand for one week before analysis. The samples were desorbed with 95% ethanol for one hour in an ultrasonic bath. The results are given below:

TIME STUDY RESULTS OF o-TOLUIDINE
(ANALYZED SAME DAY AS THE GENERATION)

	Found				Taken	
	mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
0.5X	0.635	0.649	55.8	11.63	11.72	
	0.613	0.627	54.5	11.50	11.72	
	0.615	0.629	55.4	11.35	11.72	
			mean	11.49		98.0
1X	1.136	1.162	52.2	22.26	22.60	
	1.159	1.185	53.8	22.03	22.60	
			mean	22.15		98.0
2X	2.513	2.570	55.4	46.4	46.8	
	2.482	2.538	54.8	46.3	46.8	
	2.430	2.485	54.4	45.7	46.8	
			mean	46.1		98.5

TIME STUDY RESULTS OF o-TOLUIDINE
(ANALYZED AFTER 1 WEEK OF STORAGE)

	Found				Taken	
	mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
0.5X	0.582	0.595	55.8	10.66	11.72	
	0.593	0.606	54.5	11.12	11.72	
	0.617	0.631	54.1	11.66	11.72	
			mean	11.15		95.1
1X	1.218	1.245	56.3	22.11	22.60	
	1.272	1.301	56.7	22.94	22.60	
	1.049	1.073	52.9	20.28	22.60	
			mean	21.78		96.4
2X	2.509	2.565	57.6	44.5	46.8	
	2.347	2.400	54.4	44.1	46.8	
	2.609	2.668	55.4	48.2	46.8	
			mean	45.6		97.4

From the above results, o-toluidine is stable for at least one week on silica gel. A third time study was conducted by generating six samples at 2X the OSHA standard. Three of the samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the silica gel tubes. The samples were allowed to stand for one week before analysis. The samples were desorbed with 95% ethanol for one hour in an ultrasonic bath. The results are given below:

TIME STUDY RESULTS OF o-TOLUIDINE
(FLUSHED WITH NITROGEN)

----------Found----------				Taken	
mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
2.631	2.690	55.4	48.6	46.8	
2.532	2.589	54.4	47.6	46.8	
2.736	2.798	57.6	48.6	46.8	
		mean	48.3		103.2
		(CAPPED)			
2.261	2.312	54.4	42.5	46.8	
2.462	2.517	55.4	45.4	46.8	
2.691	2.752	54.8	50.2	46.8	
		mean	46.0		98.2

From the three samples above, o-toluidine is stable on silica gel for at least one week without flushing with nitrogen.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.032$ $\overline{CV}_2 = 0.031$ $\overline{CV}_T = 0.060$

The average recovery at the OSHA standard level was 96.4%.

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: o-Toluidine S168

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.549	0.524	0.954	1.098	1.055	0.961	2.196	2.081	0.948
0.549	0.542	0.987	1.098	1.077	0.981	2.196	2.182	0.994
0.549	0.499	0.909	1.098	1.057	0.963	2.196	2.152	0.980
0.549	0.563	1.026	1.098	1.103	1.005	2.196	2.151	0.980
0.549	0.571	1.040	1.098	1.076	0.980	2.196	2.069	0.942
0.549	0.538	0.980	1.098	1.065	0.970	2.196	2.148	0.978
n =		6			6			6
mean		0.983			0.977			0.970
std dev		0.048			0.016			0.021
CV_1		0.049			0.016			0.022

$\overline{CV}_1$ 0.032

$\overline{CV}_{A+\overline{DE}}$ 0.035

The equation D.E. = $0.978 - e^{-10.27 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

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Data Sheet: o-Toluidine S168

Sampling and Analysis

Test Level	Found mg	Corr mg	Liters	mg/cu m*	Taken mg/cu m	Recovery
0.5S	0.643	0.658	55.8	11.79	11.72	
	0.615	0.630	54.5	11.56	11.72	
	0.616	0.631	55.4	11.39	11.72	
	0.618	0.633	55.8	11.34	11.72	
	0.660	0.676	54.1	12.50	11.72	
	0.596	0.611	54.5	11.21	11.72	
			n = 6			
			mean	11.63		99.2
			std dev	0.47		
			CV_2	0.040		
1S	1.227	1.255	53.8	23.33	23.44	
	1.228	1.256	56.3	22.31	23.44	
	1.256	1.284	56.7	22.65	23.44	
	1.151	1.177	52.2	22.55	23.44	
	1.203	1.230	56.7	21.69	23.44	
	1.193	1.220	52.9	23.06	23.44	
			n = 6			
			mean	22.60		96.4
			std dev	0.58		
			CV_2	0.026		
2S	2.600	2.658	55.4	48.0	46.9	
	2.384	2.438	54.4	44.8	46.9	
	2.471	2.527	54.4	46.5	46.9	
	2.542	2.599	54.8	47.4	46.9	
	2.673	2.733	57.6	47.4	46.9	
	2.547	2.604	55.4	47.0	46.9	
			n = 6			
			mean	46.8		99.8
			std dev	1.1		
$\overline{CV}_2$ 0.031			CV_2	0.024		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Acetic Anhydride, No. S170
OSHA Standard:	5 ppm (20 mg/cu m)
Chemical Used for Validation:	Acetic Anhydride J. T. Baker Chemical Company

Procedure

The procedure validated for collecting and analyzing acetic anhydride in air is described in NIOSH Method S170. The analysis is based upon the colorimetric method described in Reference No. 1. Standard samples were prepared and a standard curve was constructed by plotting absorbance versus mg of acetic anhydride. Samples of acetic anhydride were generated as described below and collected in standard midget bubblers (impingers fitted with fritted glass tipped inlet tubes) containing 10 ml of alkaline hydroxylamine. Collection efficiency tests were done at 2X the OSHA standard level. The found mg of acetic anhydride in the generated samples were determined by reading the mg found from the standard curve. The concentrations of acetic anhydride in air were determined by dividing the mg found by the sample volume (critical orifice flow rate for that sample X 107 minutes).

Modification of Reference 1

The only modification made to Reference 1 was in using a solution of equal volumes of the sodium hydroxide solution, hydroxylamine hydrochloride solution, and ferric chloride solution to dilute the samples to a final volume of 50 ml.

Generation

Samples of acetic anhydride in air were generated by the procedure described in the Backup Data Report for epichlorohydrin (Reference No. 2), and the samples were collected in standard midget bubblers containing 10 ml of the absorbing solution. The generator conditions used are given in the following table:

Nitrogen flow rate	0.125 liter/minute at 22°C
Dilution air flow rate	89.4 liters/minute at 22°C
Bath temperature	30°C

A Beckman Model 402 total hydrocarbon analyzer, which was calibrated with bag standards, was used to monitor the generated vapor concentrations during sampling (Reference No. 3). Samples were collected for 107 minutes at a rate of approximately 1.0 liter per minute (individual critical orifices vary slightly in flow rate).

Analysis

A time study at 1X of the OSHA standard level was conducted on six spiked samples. The samples were analyzed four days after preparation. No change in concentration was observed.

Collection Efficiency

The collection efficiency was determined by connecting a pair of bubblers in series at each of the six sampling ports at the 2X OSHA level, and collecting at a concentration of 37.4 mg/cu m at a rate of 1 liter per minute for 107 minutes. The solution in each bubbler was analyzed separately and the results were compared with a standard calibration curve. The mg found in the front bubbler is given in the Sampling and Analysis Data Sheet. No acetic anhydride was detected in the backup bubbler. The collection efficiency of the bubblers was found to be 1.00.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.021$ $\overline{CV}_2 = 0.032$ $\overline{CV}_T = 0.060$

The average recovery at the OSHA standard level was 102.5%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Acetic Anhydride S170

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	Recovery (%)	mg taken	mg found	Recovery (%)	mg taken	mg found	Recovery (%)
0.974	0.976	100.2	2.056	2.05	99.7	4.00	3.98	99.5
0.974	0.976	100.2	2.056	2.05	99.7	4.00	4.00	100.0
0.974	0.941	96.6	2.056	2.12	103.1	4.00	3.98	99.5
0.974	0.941	96.6	2.056	2.14	104.1	4.00	4.09	102.2
0.974	0.941	96.6	2.056	2.14	104.1	4.00	3.84	96.0
0.974	0.941	96.6	2.056	2.05	99.7	4.00	4.02	100.5
n =		6			6			6
mean		97.8			101.7			99.6
std dev		1.9			2.3			2.0
CV_1		0.019			0.023			0.020

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{DE}}$ 0.023

The equation mg found = 0.141 + 8.69 X absorbance was used as the standard curve to calculate mg found in both Analysis and Sampling and Analysis Data Sheet.

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Data Sheet: Acetic Anhydride S170

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.941	90.2	10.43	9.35	
	1.097	103.3	10.62	9.35	
	1.011	97.4	10.38	9.35	
	0.941	97.0	9.70	9.35	
	0.993	96.2	10.32	9.35	
	1.097	98.6	11.13	9.35	
		n = 6			
		mean	10.43		111.5
		std dev	0.46		
		CV_2	0.044		
1S	1.897	98.9	19.18	18.71	
	1.828	93.5	19.55	18.71	
	1.810	92.1	19.65	18.71	
	1.706	93.5	18.25	18.71	
	1.706	86.9	19.63	18.71	
	1.602	85.4	18.76	18.71	
		n = 6			
		mean	19.17		102.5
		std dev	0.57		
		CV_2	0.030		
2S	3.57	94.1	37.9	37.4	
	3.71	99.2	37.4	37.4	
	3.32	89.8	37.0	37.4	
	3.62	96.2	37.6	37.4	
	3.43	93.0	36.9	37.4	
	Sample lost due to malfunctioning orifice				
		n = 5			
		mean	37.4		100.0
		std dev	0.4		
$\overline{CV}_2$ 0.032		CV_2	0.011		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Diggle, W. M. and Gage, J. C., "The Determination of Ketene and Acetic Anhydride in the Atmosphere," Analyst, 78, 473 (1953).

2. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Sulfuric Acid, No. S174
OSHA Standard:	1 mg/cu m
Chemical used for Validation:	Sulfuric Acid Mallinkrodt Chemical Company

Procedure

The general procedure is described in NIOSH Method S174 which was adapted from P&CAM 163, a method for SO_2. The reliability of the analytical method was tested at sample concentrations equal to that present in a 180-liter sample at approximately 0.5, 1, and 2 times the OSHA standard. Appropriate aliquots (2.5, 5, and 10 µl) of a 0.37 M solution of sulfuric acid were added to 37-mm MCEF (AA) filters. Sulfuric acid was extracted from the filters with distilled water and isopropyl alcohol. The resulting solution was titrated with 0.005 M barium perchlorate using Thorin as the indicator.

Test atmospheres of sulfuric acid at concentrations at approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on the Millipore filters in closed-faced filter cassettes. The results of the analyses of these samples are given in the Sampling and Analysis table. The estimated average size of the particles was 1.5 to 2 micron diameter. The collection efficiency at 2X the OSHA standard was measured for material which might have passed through the first filter.

Modifications

Method P&CAM 163 is designed for the analysis of sulfur dioxide in air. Sulfur dioxide is collected in an oxidizing medium (0.3 N hydrogen peroxide) in a midget impinger where it is converted to sulfate anion. The pH of the sample solution is adjusted with dilute perchloric acid. Isopropyl alcohol is added to the sample solution, bringing the alcohol concentration to approximately 80% by volume. The resulting solution is titrated with 0.005 M barium perchlorate using Thorin as an indicator.

This method was adapted for use on sulfuric acid aerosol by changing the collection medium to 0.8-micron MCEF filters. The sulfuric acid particulate is collected on the filters during sampling, and analyzed after extraction with distilled water and isopropyl alcohol.

The total sample volume and the ratio of water to alcohol in the sample were both reduced from the values recommended. This procedure was necessary at the $SO_4^=$ concentrations of interest in order to sharpen the titration end point. Samples prepared according to the procedure provided changed color very gradually upon titrant addition and a definitive end point could not be established.

Generation

Samples of sulfuric acid in air were generated by the procedure in Reference No. 1. A 6 N sulfuric acid solution was used in the aspirator system. A 7.5-psig pressure drop across the aspirator would probably give particles in the size range of 1.5-2 microns. This was determined by preparation of an ammonium fluorescein solution in water which was the same weight/volume concentration as the 6 N sulfuric acid. The ammonium fluorescein was aspirated at 7.5-psig pressure drop across the aspirator tip. The aerosol droplets were spray-dried in air and the resulting particulate was collected on 0.2-micron nucleopore filters. Microscopic examination showed a mean particle size of 1.3 micron. Since sulfuric acid is extremely hygroscopic, this mean particle size is low. Sulfuric acid particles would contain an appreciable amount of water and they would probably be somewhat larger than 1.3 micron, which was the measured average diameter obtained from the dye experiments.

Prior to sample collection, it was necessary to determine the amount of dilution air in the aspirator output to produce the three desired concentration levels (0.5X, 1X, and 2X the OSHA standard level). This was necessary, because simultaneous monitoring of the generator output is not possible.

Samples were collected and analyzed to monitor the concentration in the sampling chamber prior to collection of the 2X level samples. When the correct amount of dilution air was added to give approximately the 2X level, six samples were taken.

The output of the aspirator at a 7.5 psig pressure drop was diluted with air at 42.4 liters/minute to obtain approximately the 2X level. As shown in the sampling and analysis section, the 2X level is 32% above the 2X OSHA level. Therefore, with an aspirator output of 7.5 psig, the dilution air was increased to 112 liters/minute to generate the 1X level. The 0.5X level was obtained by using 224 liters/minute of dilution air.

Collection Efficiency

Collection efficiency was determined by measuring the amount of particulates collected on each of two filters mounted back-to-back. The collection efficiency of the filter was found to be 0.967 $\pm$ 0.030 (essentially 1.0). Thus, no correction for collection efficiency was used in the calculation of results. The collection efficiency experiment was done at a generated concentration of 2.577 mg/cu m. The results are given in the following table:

COLLECTION EFFICIENCY OF SULFURIC ACID

mg/cu m in first filter	mg/cu m in backup filter	Total mg/cu m	Collection Efficiency
2.529	0.112	2.641	0.958
2.548	-0-	2.548	1.000
2.579	0.112	2.691	0.958
2.550	0.226	2.776	0.919
2.663	-0-	2.663	1.000
2.590	0.084	2.674	0.969
		mean	0.967
		std dev	0.030

Discussion

A time study at 1X the OSHA standard was conducted. Six filters were spiked with a known amount of sulfuric acid and stored for a period of five days in screw cap bottles. After five days the filters were extracted as described in NIOSH Method S174. The results of the time study are given in the following table:

mg taken	mg found	Analytical Method Recovery
0.189	0.189	1.000
0.189	0.184	0.974
0.182	0.179	0.984
0.182	0.184	1.011
0.180	0.189	1.050
0.180	0.184	1.022
	mean	1.007
	std dev	0.027

From the above results, sulfuric acid is stable on MCEF filters for a period of five days.

Several unsuccessful attempts to generate sulfuric acid aerosol were made. These attempts used sulfuric acid solutions which were less than 5% weight/volume, and an aspirator pressure drop of 7.5 psig. With ammonium fluorescein dye, it was found that a 7.5-psig pressure drop across the aspirator necessitated using at least a 5% weight/volume solution to obtain particles with diameters greater than a micron on the average.

The results of the unsuccessful generation experiments showed extremely poor collection efficiencies (less than 0.67). This was probably due to passage of submicron sulfuric acid particles through the first filter, or to wetting of the filter by water and the inherent transfer of sulfuric acid particulate from the front filter to the back filter.

Studies using ammonium fluorescein dye as described earlier in this report showed that 6 N sulfuric acid would yield an average particle size of 1.3 microns.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.055$ $\overline{CV}_2 = 0.061$ $\overline{CV}_T = 0.082$

Data Sheet: Sulfuric Acid S174

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.094	0.104	1.106	0.189	0.199	1.053	0.377	0.388	1.029
0.094	0.090	0.957	0.189	0.194	1.026	0.377	0.368	0.976
0.091	0.099	1.088	0.182	0.204	1.121	0.363	0.388	1.069
0.091	0.104	1.143	0.182	0.194	1.066	0.363	0.397	1.094
0.090	0.109	1.211	0.180	0.184	1.022	1.360	0.388	1.078
0.090	0.104	1.156	0.180	0.184	1.022	0.360	0.373	1.036
n =		6			6			6
mean		1.110			1.052			1.047
std dev		0.086			0.039			0.043
CV_1		0.077			0.037			0.041

$\overline{CV}_1$ 0.055

$\overline{CV}_{A+\overline{CE}}$ 0.059

The average Analytical Method Recovery at each level was used to calculate the corr. mg at each level in the Sampling and Analysis table.

Corrections for blanks were not made in the validation study, because the set of filters used during validation had so little sulfate, and therefore precipitate, that a true end point could not be detected.

Data Sheet: Sulfuric Acid S174

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.104	0.0937	177.1	0.529
	0.123	0.1110	179.3	0.619
	0.104	0.0937	177.1	0.529
	0.118	0.1063	175.7	0.605
	0.109	0.0982	177.1	0.554
	0.104	0.0937	176.4	0.531
			n = 6	
			mean	0.561
			std dev	0.041
			CV_2	0.073
1S	0.178	0.169	177.1	0.954
	0.187	0.178	179.3	0.993
	0.163	0.155	177.1	0.875
	0.202	0.192	175.7	1.093
	0.187	0.178	177.1	1.005
	0.187	0.178	176.4	1.009
			n = 6	
			mean	0.988
			std dev	0.072
			CV_2	0.073
2S	0.473	0.452	178.7	2.529
	0.483	0.461	180.9	2.548
	0.483	0.461	178.7	2.580
	0.473	0.452	177.3	2.549
	0.498	0.476	178.7	2.664
	0.483	0.461	178.0	2.590
			n = 6	
			mean	2.577
			std dev	0.048
$\overline{CV}_2$ 0.061			CV_2	0.019

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, o-Terphenyl, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Hydrogen Bromide, No. S175
OSHA Standard:	3 ppm (10 mg/cu m)
Chemical used for Validation:	Hydrogen Bromide lecture bottle Matheson Gas Products

Procedure

The procedure for validation of the method for collecting and analyzing concentrations of hydrogen bromide in air is described in NIOSH Method S175, which has been adapted from P&CAM 117. The reliability of the analytical method was tested at sample concentrations equal to that present in a 100-minute sample at 0.5, 1, and 2 times the OSHA standard level, when sampled at 1.0 liter per minute. The appropriate aliquot (1, 2, and 4 ml) of a 0.494 mg/ml solution of bromide ion in 0.01 N NaOH was added to 15 ml of 0.01 N NaOH and a dilution to 25 ml was made with 0.01 N NaOH. The analysis was performed using a Orion Model 94-35 bromide specific ion electrode, reference electrode Orion 90-01 single junction, and a Orion Model 407 specific ion meter (using millivolt and expanded millivolt scales). Details of the analysis procedures may be found in Section 8.4 of NIOSH Method S175.

Test atmospheres of hydrogen bromide at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected in midget bubblers containing 15 ml of 0.01 N NaOH. The results of the analyses of these samples are given in the sampling and analysis table.

Modifications

There was one major modification made to P&CAM 117. It was not necessary to use the "total ionic strength activity buffer" (TISAB) in the analysis of hydrogen bromide, because hydroxide ion does not interfere in the analysis.*

Generation

Generation of hydrogen bromide was accomplished using the apparatus described in Reference No. 1. The generation system was made entirely of Teflon. A schematic drawing is presented in Figure 1.

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* Instruction Manual for Orion Model 94-35 Bromide Specific Ion Electrode, 1971, Orion Research Inc.

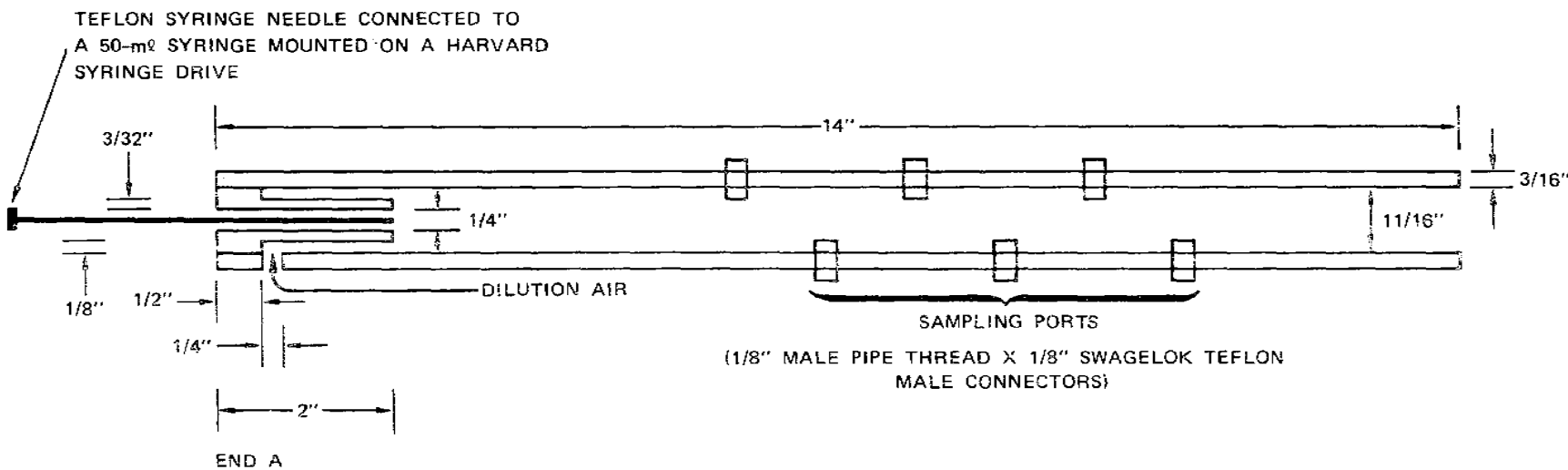

FIGURE 1 CROSS SECTION OF THE GENERATION APPARATUS FOR HYDROGEN BROMIDE

S175-2

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Six sampling ports are arranged on opposite sides of the tube at intervals of 7, 8, 9, 10, 11, and 12 inches from end A. The apparatus is placed in a hood such that the hydrogen bromide vapor exhaust does not pose a contamination hazard. Pure hydrogen bromide, contained in a 50-ml all glass syringe, is introduced into the apparatus via a 0.5-mm I.D. X 5-in long Teflon delivery tube. The syringe containing hydrogen bromide gas is mounted on a Harvard infusion/withdrawal pump and the hydrogen bromide is introduced into the Teflon dilution tube at a controlled rate. A flow rate of 0.191 ml/minute of pure hydrogen bromide (3.353 g/liter at 22°C, 763 mm Hg) out of the syringe was diluted with 31.44 liters/minute air to obtain the 2X OSHA level. This resulted in a "taken" concentration of 20.37 mg/cu m. To generate the 1X OSHA level, 62.88 liters/min of air was used which gave a "taken" concentration of 10.18 mg/cu m. At the 0.5X level, 104.38 liters/minute of dilution air gave a "taken" concentration of 6.14 mg/cu m.

Collection Efficiency

A collection efficiency experiment was performed at 20.37 mg/cu m to determine the amount of hydrogen bromide that would pass through a single midget bubbler at a flow rate of 1.0 liter/minute for a 100-minute sampling period. The experiment was performed by placing a second midget bubbler downstream of the primary bubbler. Thus, any hydrogen bromide vapor not collected in the first bubbler would be trapped in the second bubbler. The results are given in the following table:

COLLECTION EFFICIENCY OF HYDROGEN BROMIDE

mg/cu m in first bubbler	mg/cu m in second bubbler		Collection Efficiency
20.60	N.D.*		1.00
20.03	N.D.		1.00
20.07	N.D.		1.00
19.41	N.D.		1.00
21.07	N.D.		1.00
21.51	N.D.		1.00
		mean	1.00
		std dev	0

* Not detected. Limit of detection is 0.098 mg/cu m.

Collection efficiency for hydrogen bromide was determined to be 1.00, therefore no recovery correction is necessary.

Discussion

At the outset of work on hydrogen bromide, a stainless steel generation system was constructed. This system had both primary and secondary air dilution columns necessary to achieve dilution of pure hydrogen bromide gas from the lecture bottle.

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A flow of hydrogen bromide of approximately 100 ml/minute from the lecture bottle was allowed to enter the primary dilution system. Several attempts at establishing the appropriate flow rate were unsuccessful. Allowing hydrogen bromide to displace a volume of aliphatic organic solvent, such as hexane, heptane, or decane as a function of time, was not workable due to the solubility of hydrogen bromide in these solvents.

Using a calibrated rotameter was also unsuccessful. Hydrogen bromide is easily hydrated on contact with air causing the rotameter to become sticky and eventually cease functioning.

The high reactivity of hydrogen bromide necessitated measuring the flow rate of hydrogen bromide out of the lecture bottle as a function of weight loss in the lecture bottle with time. The flow rate of hydrogen bromide out of the lecture bottle can be determined for any temperature and pressure on the basis of the weight of hydrogen bromide delivered in a given time interval.

Hydrogen bromide entering the primary dilution system was immediately diluted with air. After thorough mixing in the 1-in I.D. X 2-in long stainless steel column, approximately 95% of the diluted hydrogen bromide vapor was removed by a vacuum pump. The remaining hydrogen bromide vapor enters the stainless steel secondary dilution system where a final dilution was made to reach the desired concentration levels. The stainless steel secondary dilution chamber is identical in dimension to the glass column described in Reference No. 2. The stainless steel sampling cone is the same as the one described in Reference No. 2. The major problem encountered with this system was the unexpected reactivity of hydrogen bromide vapor with stainless steel. After several unsuccessful attempts to generate a known atmosphere, the generation apparatus was disassembled for inspection. The interior of the apparatus was badly pitted and corroded. Also, a layer of bromine was found coated on the interior surfaces.

This discovery clearly explained why it was not possible to generate hydrogen bromide and collect samples with the generation apparatus described above. The majority of the generated hydrogen bromide vapor was lost by reaction on the surface of the stainless steel generation system.

At this point it was decided to replace the stainless steel generation system by one made of glass or Teflon and abandon the primary dilution system. By using a Teflon and glass generation system, it was hoped that many of the corrosion problems could be avoided. Therefore, it was decided to simply fill a syringe with pure hydrogen bromide vapor and introduce it at a very slow rate (via Harvard infusion/withdrawal pump) into the Teflon dilution apparatus previously described under the Generation Section. Addition of the proper amounts of air into the dilution system allowed generation of the three desired concentration levels.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$$\overline{CV}_1 = 0.005 \qquad \overline{CV}_2 = 0.045 \qquad \overline{CV}_T = 0.067$$

The average recovery at the OSHA standard level was 98.1%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

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Data Sheet: Hydrogen Bromide S175

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.500	0.501	1.002	1.001	0.966	0.965	2.002	2.003	1.001
0.500	0.504	1.008	1.001	0.975	0.974	2.002	2.011	1.004
0.500	0.508	1.016	1.001	0.971	0.970	2.002	2.019	1.008
0.500	0.506	1.012	1.001	0.979	0.978	2.002	2.027	1.012
0.500	0.506	1.012	1.001	0.979	0.978	2.002	2.019	1.008
0.500	0.504	1.008	1.001	0.971	0.970	2.002	2.027	1.012
n =		6			6			6
mean		1.010			0.972			1.008
std dev		0.005			0.005			0.004
CV_1		0.005			0.005			0.004

$\overline{CV}_1$ 0.005

$\overline{CV}_{A+\overline{DE}}$ 0.005

The average Analytical Method Recovery (A.M.R.) at each level is so close to 1.0 that no A.M.R. correction is needed.

Data Sheet: Hydrogen Bromide S175

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.610	97.8	6.24	6.14	
	0.634	101.4	6.25	6.14	
	0.586	99.6	5.88	6.14	
	0.563	102.6	5.49	6.14	
	0.563	96.0	5.86	6.14	
	0.541	94.8	5.71	6.14	
		n = 6			
		mean	5.90		96.1
		std dev	0.30		
		CV_2	0.051		
1S	0.990	97.8	10.12	10.18	
	1.002	101.4	9.88	10.18	
	0.978	99.6	9.82	10.18	
	0.951	102.6	9.27	10.18	
	0.994	96.0	10.35	10.18	
	0.994	94.8	10.48	10.18	
		n = 6			
		mean	9.99		98.1
		std dev	0.43		
		CV_2	0.043		
2S	2.015	97.8	20.60	20.37	
	2.031	101.4	20.03	20.37	
	1.999	99.6	20.07	20.37	
	1.991	102.6	19.40	20.37	
	2.023	96.0	21.07	20.37	
	2.039	94.8	21.51	20.37	
		n = 6			
		mean	20.45		100.4
		std dev	0.77		
$\overline{CV}_2$ 0.044		CV_2	0.038		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

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References

1. Backup Data Report, Hydrogen Fluoride, No. S176, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Hydrogen Fluoride (HF), No. S176
OSHA Standard:	3 ppm (2.45 mg/cu m)
Chemical used for Validation:	Hydrogen Fluoride made to 680 ppm in nitrogen Matheson, Coleman & Bell

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of hydrogen fluoride in air is described in NIOSH Method S176, which has been adapted from P&CAM 117. The reliability of the analytical method was tested at sample concentrations equal to that present in a 30-minute sample at 0.5, 1, and 2 times the OSHA standard level, when sampled at 1.5 liters per minute. The appropriate aliquot (1, 2, and 4 ml) of a 0.0546 mg/ml solution of fluoride ion in 0.1 N NaOH was added to 10 ml of 0.1 N NaOH and a dilution to 25 ml was made. Twenty-five ml of a total ionic strength activity buffer (TISAB) was added to prevent OH^- ion interference in the analysis. The analysis was performed using a Orion Model 94-09 fluoride specific ion electrode, reference electrode Orion 90-01 single junction, and a Orion Model 407 specific ion meter (using millivolt and expanded millivolt scales). Details of the analysis procedures may be found in Section 8.3 of NIOSH Method S176.

Test atmospheres of hydrogen fluoride at concentrations 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected in midget bubblers containing 10 ml of 0.1 N NaOH. The results of the analysis of these samples are given in the sampling and analysis table.

Modifications

One major modification was made to P&CAM 117. P&CAM 117 has recommended the use of a prefilter unit to collect particulate fluorides which may be present in the atmosphere with hydrogen fluoride vapor. The prefilter unit is connected in series to the midget bubbler which collects the hydrogen fluoride vapor. The prefilter unit was not used in the validation studies, although it has been recommended for hydrogen fluoride that one be used. The prefilter unit should not affect the collection efficiency of the midget bubbler for the collection of hydrogen fluoride vapor if a cellulose backup pad is not used in the prefilter unit (Reference No. 1).

Generation

Before generation of each of the three levels, it was necessary to check the hydrogen fluoride cylinder concentration. The apparent concentration of hydrogen fluoride in the cylinder was found to vary by as much as 10% from day to day. This variation was observed after approximately 1-1/2 weeks of allowing the stainless steel cylinder regulator to be passivated with hydrogen fluoride-nitrogen mixture.

Cylinder concentration was checked by allowing a low flow rate, which is accurately known, to bubble through two midget bubblers (fitted with Teflon gas delivery tubes) in series for a specified time. The solution in each of the two bubblers was analyzed separately with the fluoride specific ion electrode. From the amount of fluoride ion found, and the flow rate of hydrogen fluoride out of the cylinder, the concentration of hydrogen fluoride in the cylinder was calculated. For the 2X and 1X level sample collections, the cylinder concentration was found to be 410 mg/cu m of hydrogen fluoride. For the 0.5X sample generation, the concentration delivered from the cylinder was found to be 440 mg/cu m. This reflects continued losses due to the stainless steel cylinder regulator.

At the 2X OSHA level, a flow rate out of the hydrogen fluoride cylinder was set at 244 ml/min. This flow was diluted with 22.01 liter/minute of air to give a "taken" concentration of 4.50 mg/cu m. At the 1X OSHA level, the flow out of the cylinder was 267 ml/min, and the dilution air was 42.09 liter/minute. This gave a "taken" concentration of 2.584 mg/cu m. At the 0.5X level, a cylinder flow rate of 240 ml/min and dilution air of 79.20 liter/minute gave a taken level of 1.329 mg/cu m.

The generation apparatus was made entirely of Teflon. A schematic drawing is presented in Figure 1.

Six sampling ports are arranged on opposite sides of the tube at intervals of 7, 8, 9, 10, 11, and 12 inches from end A. The apparatus is placed in a hood such that the hydrogen fluoride vapor exhaust does not pose a contamination hazard. Hydrogen fluoride is introduced into the apparatus from the cylinder via a 1/4-in. O.D. Teflon tube. The entire system was passivated for approximately one day with the hydrogen fluoride-nitrogen mixture from the cylinder. Six samples at each of the three levels were collected in midget bubblers containing 10 ml of 0.1 N NaOH. Samples were collected for 30 minutes at a rate of approximately 1.5 liters per minute (individual critical orifices vary slightly in flow rate).

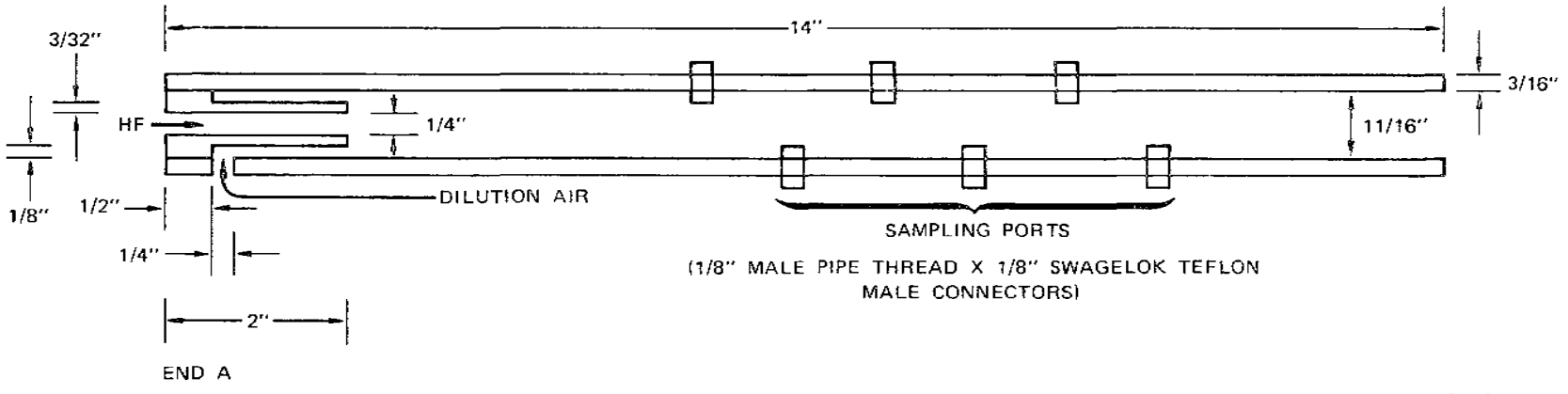

FIGURE 1 CROSS SECTION OF THE GENERATION APPARATUS FOR HYDROGEN FLUORIDE

Collection Efficiency

A collection efficiency experiment was performed at 4.50 mg/cu m to determine the amount of hydrogen fluoride that would pass through a single midget bubbler at a flow rate of 1.5 liter/minute for a 30-minute sampling period. The experiment was performed by placing a second midget bubbler downstream of the primary bubbler. Thus, any hydrogen fluoride vapor not collected in the first bubbler would be trapped in the second bubbler. The results are given below:

COLLECTION EFFICIENCY RESULTS FOR HYDROGEN FLUORIDE (HF)

HF in 1st bubbler (mg/cu m)	HF in 2nd bubbler (mg/cu m)	Total amount (mg/cu m)	Collection Efficiency
4.70	0.06	4.76	0.987
4.46	0.02	4.48	0.996
4.45	0.02	4.47	0.996
4.48	0.03	4.51	0.993
4.40	0.06	4.46	0.987
4.38	0.05	4.43	0.989
		mean	0.991
		std dev	0.004

A collection efficiency of 0.991 $\pm$ 0.004 was determined for hydrogen fluoride; therefore, no recovery correction is necessary.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.017$ $\overline{CV}_2 = 0.026$ $\overline{CV}_T = 0.057$

The average recovery at the OSHA standard level was 105.5%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Hydrogen Fluoride S176

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.0550	0.0537	0.976	0.1099	0.1118	1.017	0.2198	0.2197	1.000
0.0550	0.0527	0.958	0.1099	0.1144	1.041	0.2198	0.2156	0.981
0.0550	0.0541	0.984	0.1099	0.1139	1.036	0.2198	0.2156	0.981
0.0550	0.0533	0.969	0.1099	0.1118	1.017	0.2198	0.2139	0.973
0.0550	0.0560	1.018	0.1099	0.1118	1.017	0.2198	0.2180	0.992
0.0550	0.0560	1.018	0.1099	0.1126	1.025	0.2198	0.2197	1.000
n =		6			6			6
mean		0.987			1.026			0.988
std dev		0.025			0.011			0.011
CV_1		0.025			0.011			0.011

$\overline{CV}_1$ 0.017

$\overline{CV}_{A+\overline{DE}}$ 0.018

The average A.M.R. at each level is so close to 1.0 that no A.M.R. correction is needed.

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Data Sheet: Hydrogen Fluoride S176

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.0567	44.3	1.280	1.329	
	0.0579	44.8	1.292	1.329	
	0.0579	44.3	1.307	1.329	
	0.0614	43.9	1.399	1.329	
	0.0614	44.3	1.386	1.329	
	0.0591	44.1	1.340	1.329	
		n = 6			
		mean	1.334		100.4
		std dev	0.050		
		CV_2	0.037		
1S	0.1210	44.3	2.731	2.584	
	0.1210	44.8	2.701	2.584	
	0.1210	44.3	2.731	2.584	
	0.1210	43.9	2.756	2.584	
	0.1210	44.3	2.731	2.584	
	0.1190	44.1	2.698	2.584	
		n = 6			
		mean	2.725		105.5
		std dev	0.022		
		CV_2	0.008		
2S	0.205	44.3	4.63	4.50	
	0.198	44.8	4.42	4.50	
	0.195	44.3	4.40	4.50	
	0.195	43.9	4.44	4.50	
	0.193	44.3	4.36	4.50	
	0.191	44.1	4.33	4.50	
		n = 6			
		mean	4.43		98.4
		std dev	0.11		
$\overline{CV}_2$ 0.026		CV_2	0.025		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Jahr, J., "A New Dual Filter Method for Separate Determination of Hydrogen Fluoride and Dustlike Fluorides in Air," Staub-Reinhalt der Luft, 32, No. 6, 17, June 1972.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: 2-Hexanone, No. S178

OSHA Standard: 410 mg/cu m

Chemical used for validation: 2-Hexanone, Aldrich, Certified

Procedure

The general procedure used is described in NIOSH method No. S178 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of 2-hexanone represented in a 10-liter air sample. The charcoal used was Lot 105 activated coconut charcoal, with 100-mg front and 50-mg backup sections, supplied by SKC, Inc. Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using decane as internal standard The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures amy be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 79.2 mg/min. of 2-hexanone via a syringe injector to a dry air stream flowing at a rate of 0.1003 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liter per minute for 44 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 35 mg of 2-hexanone when a test atmosphere containing 790 mg/cu m of 2-hexanone in air was sampled at 0.187 liter per minute for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0184$ $\overline{CV}_2 = 0.0167$ $\overline{CV}_T = 0.0533$

The average recovery of the generated samples over all levels was 99.6%.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

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Data Sheet: 2-Hexanone, S178

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.099	1.542	0.735	4.04	3.26	0.807	8.07	6.94	0.860
2.099	1.673	0.797	4.04	3.19	0.790	8.07	6.79	0.841
2.099	1.624	0.774	4.04	3.28	0.812	8.07	6.75	0.836
2.099	1.641	0.782	4.04	3.28	0.812	8.07	6.74	0.835
2.099	1.600	0.762	4.04	3.28	0.812	8.07	6.82	0.845
2.099	1.638	0.780	4.04	3.22	0.797	8.07	6.78	0.840
n =		6			6			6
mean		0.772			0.805			0.843
std dev		0.0213			0.0094			0.0092
CV_1		0.0276			0.0117			0.0109
			$\overline{CV}_1$		0.0184			
			$\overline{CV}_{A+\overline{DE}}$		0.0199			

Data Sheet: 2-Hexanone, S178

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.425	1.863	9.85	189.1	188.2	
	1.358	1.775	9.94	178.6	188.2	
	1.400	1.830	9.90	184.8	188.2	
	1.420	1.856	10.11	183.6	188.2	
	1.384	1.809	9.72	186.1	188.2	
	1.377	1.800	9.85	182.7	188.2	
			n = 6			
			mean	184.2		97.9
			std dev	3.52		
			CV_2	0.0191		
1S	3.19	3.99	9.94	401	388	
	3.11	3.89	9.90	393	388	
	3.08	3.85	10.11	381	388	
	3.03	3.79	9.94	381	388	
	3.12	3.90	9.94	392	388	
	3.12	3.90	9.94	392	388	
			n = 6			
			mean	390		100.5
			std dev	7.75		
			CV_2	0.0199		
2S	5.49*	6.61*	9.85	671*	790	
	6.66	7.93	9.94	798	790	
	6.89	8.20	10.33	794	790	
	6.62	7.88	9.94	793	790	
	6.58	7.83	9.94	788	790	
	6.62	7.88	9.90	796	790	
			n = 5			
			mean	794		100.5
			std dev	3.77		
			CV_2	0.0047		
			$\overline{CV}_2$	0.0167		

*These values excluded from statistical analysis

Backup Data Report

Substance: Phthalic Anhydride, No. S179

OSHA Standard: 12 mg/cu m

Chemical Used for Validation: Phthalic Anhydride, Fisher Scientific Co., Certified

Discussion

Preliminary studies were conducted to develop a high performance liquid chromatographic (HPLC) method of analysis for phthalic anhydride and also to test the sample collection method on Type AA Millipore filters.

In the development of an HPLC method, several types of adsorbent and solvent system combinations were tried to chromatograph both phthalic anhydride and phthalic acid. The pellicular packings tried consisted of Corasil II, Permaphase ETH and Permaphase ODS (reversed phase chromatography), and Sepcote AN-40 (anion exchange pellicular media). The range of solvent systems tried included: (a) methylene chloride, chloroform, acetonitrile, ethyl acetate, methanol and gradient systems from methylene chloride to methanol to water for normal-partition chromatography on Corasil II; (b) gradient systems from water to methanol to methylene chloride for reversed phase chromatography; and (c) a wide range of buffered systems at varying pH (1 to 6.5) for the anion exchange resin. Early results indicated that it would be difficult to chromatograph the anhydride because of problems related to solubility and hydrolysis to the free acid or the half-ester/half-acid. Thus, subsequent efforts were directed towards chromatography of the free acid, for which studies phthalic acid (Fisher Scientific, Inc., Reagent Grade) was used. Aqueous solutions of phthalic acid could be chromatographed on Sepcote AN-40 using a chloride system but in solutions of high ionic strength, which would be the case encountered for the complete and rapid hydrolysis of the phthalic anhydride, irreproducible results were obtained.

A successful HPLC method was developed for phthalic acid using a microparticle adsorbent, Partisil™ 10 (silica, 10 microns, Whatman/Reeve-Angel) using the solvent system described in the Procedure Section. Again, attempts to chromatograph phthalic anhydride failed in that a solvent gradient from a non-polar to polar solvent did not elute phthalic anhydride while the use of a polar solvent like methanol in the isocratic mode eluted phthalic anhydride with the solvent front. The results indicate that phthalic anhydride may be gradually decomposing on the silica column in the first instance cited. In the second case, the phthalic anhydride may have already reacted with the methanol to form the half-ester/half-acid.

The generation and collection method was also tested to verify whether any phthalic anhydride vapor was also produced with the particulate.

A set of six samples was collected such that 3 filters were backed up by secondary filters while 3 other filters were backed up by impingers containing 10 ml or 0.1 M hydrochloric acid. This HCl concentration was used for collection by Bumsted (Reference 2). The results summarized in Table 1 show that no phthalic acid was found in the backup impingers while 5.7% was found in the backup filters. Note that the difference is not due to sensitivity because the sample aliquots taken for the backup filters were adjusted to be equivalent to the concentration of the corresponding backup impingers assayed. The absence of phthalic acid in the backup impingers can be interpreted to mean that no vapors were co-generated and that the particle size generated may not be the right size for efficient collection in the impingers.

Procedure

The general procedure used is described in NIOSH Method No. S179. The analyte is collected as a particulate on 37 mm Tvpe AA Millipore filters, extracted from the filter and hydrolyzed with 0.2 N ammonium hydroxide and assayed as phthalic acid by high-pressure liquid chromatography (HPLC) on a microparticle silica column. The solvent system used for chromatographic separation was a mixture of acetic acid/methanol/methylene chloride. The solvent flow rate was maintained at 0.8 ml per minute. The liquid chromatograph used consisted of a Milton-Roy mini-pump with a Laboratory Data Control (LDC) Pulse Dampener (Model 709) an LDC 20 µl loop injector (stainless steel), a stainless steel column (25 cm x 4.6 mm I.D.) packed with Partisil^{tm} 10, and an LDC 254 nm UV Detector, (Model 1205).

The reliability of the analytical method was tested at sample concentrations equal to that present in a 100-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of a freshly prepared solution of the analyte in acetone and isopropyl alcohol was added to 37 mm Type AA Millipore filters and analyzed as described in detail in Section 8.4 of NIOSH Method No. S179.

It is important to note that when solutions of phthalic anhydride in ethylacetate were used to prepare spiked samples by adding 100 to 400 µl aliquots of the solution to Type AA Millipore filters, the recovery values obtained ranged from 10-40%. This low recovery is due to the fact that the ethylacetate reacts with the filter and renders the "free" phthalic anhydride inaccessible to the extracting solvent. The only solvent system found to be suitable to meet the requirements of phthalic anhydride solubility and cellulose membrane filter compatibility is a solution of phthalic anhydride in a mixture of acetone and isopropyl alcohol as described in detail in Section 8.5.2 of NIOSH Method S179. Limited data indicate that the solution is not stable and that the phthalic anhydride content of the solution after 1, 2 and 15 hours are respectively 95, 90, and 40%. The anhydride probably decomposes to the half-ester/half-acid as supported by a progressive increase with time of a chromatographic peak eluting earlier than the phthalic acid component.

Table 1

Comparison of Phthalic Anhydride Collected
on Backup Filter vs. Backup Impinger

Test Concentration: 14 mg/cu m

A. Collection on Front Filter with Backup Filter

µg Found			% Found
Front Filter	Backup Filter	Total	in Backup Filter
1205	75	1280	5.9
1210	65	1275	5.1
1180	75	1255	6.0

Average Found in Backup Filter . . . 5.7%

B. Collection on Front Filter with Backup Impinger (10 ml 0.1 N HCl/Water)

µg Found			% Found
Front Filter	Backup Impinger	Total	in Backup Impinger
1150	0	1150	0
1175	0	1175	0
1115	0	1115	0

Average Found in Backup Impinger . . 0%

For the set of 18 analytical samples reported (Table 3), a fresh solution of phthalic anhydride in acetone and isopropyl alcohol was used for each set of six samples per concentration level. In each case, the filters were spiked within one hour after the phthalic anhydride solutions were prepared.

Modification

Only the sample collection part of this method has been adapted from a previously described method, P&CAM 173. The analytical procedure described has been developed to satisfy the specific requirements for phthalic anhydride and is a derivation of the direct UV analysis of phthalic acid described by Bumsted in Reference 2.

Generation

Test atmosphere samples at a concentration 2X, 1X and 0.5X the OSHA standard level were generated by spray drying a solution of phthalic anhydride in ethylacetate using the DeVilbiss Model 3A Ultrasonic Nebulizer. The generation assembly is described in the Molybdenum (Insoluble Compounds), S376 Backup Data Report. Some problems were encountered with dilution ratios in the simultaneous generation of the three target concentrations for phthalic anhydride. Thus, the 18 samples reported were taken from three separate generation attempts but the six samples reported for a given test level were collected simultaneously at 1.5 liters per minute for 67 minutes (100 liters). The phthalic anhydride concentration of the solutions used for generation varied from 13 to 22 g per liter of ethylacetate. Based upon the data typically reported in the literature for this type of generation system and solution concentration, an estimate of the particulate generated was in the 1-10 micron size range. Other pertinent details of the sample generation and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for phthalic anhydride was determined based on the data for two sets of six collected samples representing air sample concentrations of 17 and 50 mg/cu m. The assembly of the filter series was such that the front and backup filters were physically separated and only the backup filter was supported by the backup pad. The average collection efficiency found was 94% for the 17 mg/cu m series and 98% for the 50 mg/cu m series (Table 2).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0397$ $\overline{CV}_2 = 0.0718$ $\overline{CV}_T = 0.089$

Table 2

Collection Efficiency of Phthalic Anhydride, S179

Test Concentration	---µg Found on Filter-----			
mg/cu m	Front	Backup	Total	% Collection Efficiency
16.9	1553	89	1642	94.6
	1591	125	1716	92.7
	1549	101	1650	93.9
	1569	121	1690	92.8
	1640	109	1749	93.8
	1568	107	1675	93.6
		Average		93.6
49.9	4820	122	4942	97.5
	Sample lost			
	5050	98	5148	98.1
	4940	115	5055	97.7
	4780	125	4905	97.5
	4760	119	4879	97.6
		Average		97.7

Overall Average Collection Efficiency = 95.7

7.11<

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Bumsted, H.E., and W.L. Doyle, "Determination of Airborne Maleic Anhydride, Maleic Acid, Phthalic Acid and Anhydride Combined, and Fumaric Acid," Paper Presented at Industrial Health Conference, Boston, May 24, 1973.

Table 3

Data Sheet: Phthalic Anhydride, S179

Analysis*

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
568	554	0.975	1100	966	0.878	2227	2246	1.009
568	596	1.049	1100	1090	0.991	2227	2326	1.044
568	589	1.037	1100	1061	0.965	2227	2235	1.004
568	593	1.004	1100	1020	0.927	2227	2056	0.923
568	556	0.979	1100	1053	0.957	2227	2304	1.035
568	564	0.993	1100	1064	0.967	2227	2264	1.017
n =		6			6			6
mean		1.013			0.948			1.005
std dev		0.0342			0.0398			0.0431
CV_1		0.0337			0.0420			0.0429

$\overline{CV}_1$ 0.0397

$\overline{CV}_{A+\overline{DE}}$ 0.0429

* All spikings were done with fresh solutions of phthalic anhydride, i.e., the solutions were used within one hour after preparation.

Data Sheet: Phthalic Anhydride, S179

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	580	101.3	5.73
	607	101.5	5.98
	455	100.9	4.51
	590	101.7	5.80
	526	102.2	5.15
	592	101.6	5.83
		n = 6	
		mean	5.50
		std dev	0.563
		CV_2	0.1024
1S	1205	101.4	11.88
	1150	101.3	11.35
	1210	101.3	11.94
	1175	101.3	11.60
	1180	101.1	11.67
	1115	100.1	11.14
		n = 6	
		mean	11.60
		std dev	0.308
		CV_2	0.0265
2S	*	101.3	*
	3120	101.2	30.8
	2984	101.3	29.5
	2680	101.2	26.5
	2820	101.0	27.9
	2750	102.1	26.9
		n = 5	
		mean	28.3
		std dev	1.806
		CV_2	0.0638
		$\overline{CV}_2$	0.0718

*Sample lost

Backup Data Report

Substance:	Tin, Inorganic Compounds Except Oxides, No. S183
OSHA Standard:	2 mg/cu m
Chemical Used for Validation:	Tin Chloride Bakers Analyzed Reagent

Procedure

The general procedure is described in NIOSH Method No. S183 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations representing 250-liter samples at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of a solution of tin in dilute hydrochloric acid was added to 37-mm/0.8-micron Type AA Millipore filters. The filters containing the samples were digested with concentrated nitric and sulfuric acids and the analyte dissolved in hydrochloric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer. The absorbance, measured at 224.6 nm, was used as a measure of the tin concentration in the sample. A similar procedure was used for the analysis of eighteen generated samples, six each at approximately 0.5, 1, and 2 times the OSHA standard level. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S183.

Modification

P&CAM 173 was modified by use of sulfuric acid to aid in decomposition of the filter material and to prevent formation of insoluble tin oxides.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the NIOSH Nickel Report (Reference No. 1). Concentrations of 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing solutions of tin chloride in dilute hydrochloric acid at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of approximately 1.4 liters per minute for 180 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate tin was determined by collecting eight filter samples at an air sample concentration of 4.3 mg/cu m (2X OSHA standard level). The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was 1.00 when the test atmosphere was sampled for 180 minutes. Therefore, no correction for collection efficiency is necessary.

Collection Efficiency

2S Level

Micrograms Found Front Filter	Micrograms Found Backup Filter	Collection Efficiency
1175	N.D.	1.00
1120	N.D.	1.00
1135	N.D.	1.00
1165	N.D.	1.00
1175	N.D.	1.00
1185	N.D.	1.00
1180	N.D.	1.00
1055	N.D.	1.00

N.D. = Not Detected (less than 10 micrograms)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.018$ $\overline{CV}_2 = 0.022$ $\overline{CV}_T = 0.055$

Data Sheet: Tin, Inorganic Compounds Except Oxides S183

Analysis

Level	0.5S			1S			2S	
µg added	µg found	A.M.R.	µg added	µg found	A.M.R.	µg added	µg found	A.M.R.
270	285	1.056	540	567	1.050	1080	1143	1.058
270	292	1.082	540	592	1.096	1080	1145	1.060
270	285	1.056	540	573	1.061	1080	1168	1.082
270	285	1.056	540	573	1.061	1080	1168	1.082
270	280	1.037	540	565	1.046	1080	1180	1.093
270	275	1.018	540	585	1.083	1080	1170	1.083
n =		6			6			6
mean		1.051			1.066			1.076
std dev		0.022			0.019			0.014
CV_1		0.021			0.018			0.013

$\overline{CV}_1$ 0.018

$\overline{CV}_{A+\overline{AMR}}$ 0.019

An average Analytical Method Recovery (A.M.R.) correction of 1.064 was used to calculate the corr. µg in the Sampling and Analysis Table.

Data Sheet: Tin, Inorganic Compounds Except Oxides S183

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.265	0.249	252.9	0.985
	0.250	0.235	252.0	0.933
	0.245	0.230	252.0	0.913
	0.255	0.240	252.0	0.952
	0.245	0.230	251.1	0.916
	0.250	0.235	252.0	0.933
			n = 6	
			mean	0.939
			std dev	0.027
			CV_2	0.029
1S	0.530	0.498	252.9	1.969
	0.515	0.484	252.0	1.921
	0.525	0.493	252.0	1.956
	0.520	0.489	252.0	1.940
	0.520	0.489	251.1	1.947
	0.525	0.493	252.0	1.956
			n = 6	
			mean	1.948
			std dev	0.017
			CV_2	0.009
2S	1.175	1.104	252.9	4.37
	1.120	1.053	252.0	4.18
	1.135	1.067	252.0	4.23
	1.165	1.095	252.0	4.35
	1.175	1.104	251.1	4.40
	1.185	1.114	252.0	4.42
			n = 6	
			mean	4.32
			std dev	0.10
$\overline{CV}_2$ 0.022			CV_2	0.023

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

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References

1. Backup Data Report, Nickel, No. S206, prepared under Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under Contract No. CDC-99-74-45.

Backup Data Report

Substance: Zirconium Compounds (as Zr), No. S185

OSHA Standard: 5 mg/cu m

Chemical used for Validation: Zirconium oxychloride, $ZrOCl_2 \cdot 8H_2O$, Fisher Scientific Co., certified

Procedure:

The general procedure used is described in NIOSH Method No. S185 which is a modification of P&CAM 173 for filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equal to that present in a 720-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in water was added to 37 mm Type AA Millipore filters. The analyte was recovered from the filter by digestion with concentrated nitric acid and perchloric acid. The resulting solution of the analyte is analyzed with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The absorbance, measured at 360.1 nm, was used as a measure of zirconium concentration in the sample. Appropriate standard solutions were analyzed alternately with samples to minimize observed variations in flame responses during any given day. Similarly, the 18 generated samples (6 at each of the 0.5, 1 and 2X OSHA standard levels) were analyzed accordingly. Details of the digestion and analytical procedures may be found in Section 8.3 of NIOSH Method No. S185.

Modification

P&CAM 173 was modified as follows. Digestion with nitric and perchloric acid is recommended to ensure total digestion of the filter. Undigested cellulose matrix interferes with the assay and low recoveries are obtained when only the nitric acid digestion route is employed. Likewise, the addition of ammonium fluoride is necessary to enhance the measurable signal. The analysis procedure was also modified such that a calibration curve was not used, instead samples were analyzed alternately with standards. This procedure is necessary because it has been observed that there is a marked decrease in the slope of the calibration curve obtained at the beginning of the day as compared to subsequent calibration runs. These variations are believed to be due to carbon buildup at the burner head.

Discussion

A few initial experiments with zirconium sulfate gave essentially no response. Presumably this was due to suppression of the signal by sulfate since upon addition of lanthanum (as the chloride) some signal for zirconium was observed. Because of anticipated problems, with work with the sulfate was not pursued further. All further experiments were carried out using zirconium oxychloride and all data reported have been obtained using this compound.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous zirconium oxychloride solution containing 120 g/liter as zirconium into a dry, solvent-free air stream flow. The atomizer flow rate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the three test levels were collected simultaneously at 1.5 liters per minute for 480 minutes (720 liters). Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate zirconium compounds was determined by collecting six filter samples at air sample concentrations of 9.0 mg/cu m. The physical layout of the filter series (front and backup) used for each of the two sets of six samples collected was such that the two filters were mounted back to back in contact with each other and supported by the backup pad. The average collection efficiency found was 100% (Table 1).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0234$ $\overline{CV}_2 = 0.0155$ $\overline{CV}_T = 0.053$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Collection Efficiency: Zirconium Compounds (as Zr)

µg Found			
Front	Backup*	Total	% Collected in front
6570	ND	6570	100.0
6480	ND	6480	100.0
6600	ND	6600	100.0
6510	ND	6510	100.0
6600	ND	6600	100.0
6600	ND	6600	100.0

Average Collection Efficiency . . . . 100.0%[Δ]

*ND = no detectable Zr; the lower limit of detection is 400 µg/25 ml.

[Δ]The collection efficiency, on the basis of the known detection limit and the average amount found in front filters, may be expressed as >94%.

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Data Sheet: Zirconium Compounds (as Zr), S185

Analysis

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
1848	1850	1.001	3700	3725	1.007	7260	7900	1.088
1848	1850	1.001	3700	3650	0.986	7260	7900	1.088
1848	1850	1.001	3700	3650	0.986	7260	7500	1.033
1848	1925	1.042	3700	3725	1.007	7260	7800	1.074
1848	1825	0.988	3700	3650	0.986	7260	7625	1.050
1848	1750	0.947	3700	3650	0.986	7260	7500	1.033
n =		6			6			6
mean		0.997			0.993			1.061
std dev		0.0305			0.0108			0.0258
CV_1		0.0306			0.0109			0.0243

$\overline{CV}_1$ 0.0234

$\overline{CV}_A + \overline{CE}$ 0.0253

Data Sheet: Zirconium Compounds (as Zr), S185

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	1588	726	2.187
	1482	723	2.050
	1575	720	2.188
	1540	725	2.124
	1558	722	2.158
	1552	728	2.132
		n = 6	
		mean	2.140
		std dev	0.0515
		CV_2	0.0241
1S	3210	727	4.42
	3230	728	4.44
	3180	724	4.39
	3240	729	4.44
	3190	733	4.35
	3220	728	4.42
		n = 6	
		mean	4.41
		std dev	0.0346
		CV_2	0.0079
2S	6570	727	9.04
	6480	726	8.93
	6600	726	9.09
	6510	726	8.97
	6600	724	9.12
	6600	738	8.94
		n = 6	
		mean	9.02
		std dev	0.0802
		CV_2	0.0089
		$\overline{CV_2}$	0.0155

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Backup Data Report

Substance: Copper Dusts and Mists, No. S186

OSHA Standard: 1.0 mg/cu m

Chemical Used for Validation: Anhydrous Cupric Sulfate, Fisher Scientific Company, certified

Procedure

The general procedure used is described in NIOSH Method No. S186 which is an application of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 90-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of an aqueous solution of the analyte was added to 37 mm Type AA Millipore filters. The sample-containing filters were digested with concentrated nitric acid and the analyte solubilized with hydrochloric acid. Analyses were done with a Perkin-Elmer Model 303 Atomic Absorption Spectrometer. The absorbance, measured at 324.7 nm was used as a measure of the copper concentration in the sample. Appropriate standard solutions were analyzed on the same day the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S186.

Modification

There was no major modification of P&CAM 173.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of cupric sulfate containing 12 g/liter as copper into a dry solvent-free air stream flow. The atomizer flowrate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 60 minutes (90 liters). Since collection efficiency was found to be 1.00 ± 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

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Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate copper was determined by collecting six filter samples at an air sample concentration of 1.8 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency was 99.6% when the test atmosphere was sampled for 60 minutes (Table 1).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0122 \qquad \overline{CV}_2 = 0.00927 \qquad \overline{CV}_T = 0.0511$$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Table 1

Collection Efficiency: Copper Dusts and Mists

Test Concentration	µg Found on Filter			% Found on Front
	Front	Backup	Total	
1.83 mg/cu m	166.5	<0.7	166.5	100
	165.0	2.5	167.5	98.5
	169.2	0.7	169.9	99.6
	166.5	1.2	167.7	99.3
	164.0	<0.7	164.0	100
	166.7	<0.7	166.7	100

Average Collection Efficiency 99.6%

Data Sheet: Copper Dusts and Mists S186

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
45.0	46.2	1.027	90.0	91.2	1.013	180.0	173.2	0.962
45.0	46.7	1.038	90.0	91.7	1.019	180.0	177.2	0.984
45.0	45.4	1.009	90.0	92.2	1.024	180.0	179.2	0.996
45.0	46.7	1.038	90.0	91.2	1.013	180.0	178.2	0.990
45.0	45.4	1.009	90.0	93.7	1.041	180.0	176.2	0.979
45.0	46.7	1.038	90.0	91.7	1.019	180.0	175.2	0.973
n =		6			6			6
mean		1.027			1.021			0.981
std dev		0.0142			0.0104			0.0122
CV_1		0.0138			0.0102			0.0124

$\overline{CV}_1$ 0.0122

$\overline{CV}_{A+\overline{DE}}$ 0.0132

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Data Sheet: Copper Dusts and Mists S186
Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m
0.5S	42.8	90.7	0.472
	42.3	90.3	0.468
	42.3	90.0	0.470
	42.8	90.5	0.473
	43.0	90.2	0.477
	42.3	91.0	0.465
		n = 6	
		mean	0.471
		std dev	0.00417
		CV_2	0.00885
1S	85.7	90.8	0.945
	84.7	90.9	0.933
	84.7	90.4	0.938
	85.5	91.1	0.939
	84.7	91.5	0.927
	85.2	91.0	0.937
		n = 6	
		mean	0.937
		std dev	0.00606
		CV_2	0.00647
2S	166.5	90.8	1.834
	165.0	90.7	1.819
	169.3	90.7	1.867
	166.5	90.7	1.836
	164.0	90.5	1.812
	166.8	92.2	1.809
		n = 6	
		mean	1.830
		std dev	0.0215
		CV_2	0.0117
		$\overline{CV_2}$	0.00927

Backup Data Report

Substance: Tellurium Hexafluoride, No. S187

OSHA Standard: 0.2 mg/cu m

Chemical Used for Validation: Tellurium Hexafluoride, 99%, Ozark Mahoning Co., 1870 South Boulder, Tulsa, Oklahoma, 74119

Procedure

The general procedure used is described in NIOSH Method No. S187 which has been adapted in part from P&CAM 127 for the collection of vapors on charcoal and in part from P&CAM 173 for the analysis of metals by atomic absorption. The charcoal used was Lot 105 activated coconut charcoal, with 100-mg front and 50-mg backup sections, supplied by SKC, Inc., Pittsburgh, Pa. Desorption efficiency tests were carried out by adding known amounts of tellurium hexafluoride gas to the charcoal tubes as described in detail in the discussion section. The samples were desorbed in 10 ml of 0.01 N sodium hydroxide. The appropriate DE correction factor used was determined from the "hand drawn" DE curve. The samples were analyzed in a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 503, equipped with a tellurium electrodeless discharge lamp. The samples were atomized into an air-acetylene flame and the absorbance at 214.3 nm was used as a measure of tellurium or tellurium hexafluoride by using the molecular weight factor. The tellurium standard stock solution (1000 ppm) was from Fisher Scientific. A detailed description of the analytical procedure may be found in NIOSH Method No. S187 and a description of the vapor generator and dilution system may be found in the Butyl Acetate S47 Backup Data Report and Attachment.

Modification

The original method suggested for the analysis of tellurium hexafluoride involved a separate assay of tellurium by atomic absorption and of fluoride by an ion-specific electrode. It was recognized, however, that the fluoride assay by ion-specific electrode at the concentration levels of interest would be cumbersome and the required mass balance for the two elements might not be obtainable. In addition, the physical state of tellurium hexafluoride allows for collecting this analyte separately from other particulate tellurium compounds although other gaseous tellurium compounds, like H_2Te and Te_2F_{10}, might interfere; this interference was not tested specifically. The sampling procedure tested called for the use of a cellulose membrane filter to collect particulate tellurium compounds followed by a charcoal tube to collect tellurium hexafluoride.

To prove the applicability of this approach, six samples were collected in a sampling arrangement which included a train of a filter cassette holder containing a 37-mm Type AA Millipore filter supported by a cellulose pad and a charcoal tube containing the front 100 mg

and the 50-mg backup section. Each portion of the sampling train, i.e., front filter, pad, charcoal, were then analyzed separately by extracting with 0.01 N NaOH and analyzing for tellurium by atomic absorption. For each of these six samples no tellurium was found in extracts of the filter and of the pad; the total tellurium was found in the 100-mg section of the charcoal tube as shown in Table 1. This sampling train arrangement is recommended for tellurium hexafluoride. The generator concentration for this experimental study was equivalent to 2X OSHA standard level.

Discussion

Preliminary experiments were conducted by testing the desorption of tellurium hexafluoride from 100 mg of charcoal using 10 ml of the following solvents: 0.01 N HNO_3, 0.1 N HNO_3, 0.01 N NaOH, 0.1 N NaOH. For each solvent cited, duplicate samples loaded with 42 µg of tellurium hexafluoride were analyzed. The samples were desorbed in 10 ml of solvent and the desorption efficiencies found were:

0.01 N HNO_3	0.1 N HNO_3	0.01 N NaOH	0.1 N NaOH
0.596	0.683	0.933	0.847
0.690	0.736	0.906	0.832

All subsequent experiments were conducted using 0.01 N NaOH for desorption.

In order to determine sample stability, two sets of 18 analytical samples were prepared by adding an amount of tellurium hexafluoride to 100 mg of Lot 105 charcoal. The two sets of spiked samples were prepared similarly but a different gas stock standard was used during a two-day period. The amount of analyte added was equivalent to that present in a 380-liter sample at 0.5, 1 and 2X the OSHA standard. The gas stock standard was prepared by adding 50 ml of pure tellurium hexafluoride in a gas-tight syringe to an evacuated 263-ml gas bulb and opening the stopcocks to allow dilution with air and equilibration to atmospheric pressure. Aliquots of this gas standard--20, 40 and 80 µl--were slowly added to the charcoal tube (100-mg front and 50-mg backup). After the spiking process, the backup sections of the charcoal tubes were removed and random duplicates representative of each of the 3 test levels were analyzed in order to check whether the tellurium hexafluoride was totally added only to the front 100-mg section of charcoal. No tellurium hexafluoride was found in any of the six backup sections analyzed.

The data for these two sets of analytical samples are summarized in Tables 2 and 3 for the 1-day and 5-day-old samples respectively. The data appeared to indicate some decrease in desorption efficiency with time; however, some uncertainties were raised due to the fact that these samples were prepared using two different gas stock standards on different days. Although appropriate pressure

TABLE 1

Analytical Data on Sampling Train for Tellurium Hexafluoride
Sampling Rate: 1.1 liters per minute

µg Found				Sample Volume	
Filter	Pad	Front Charcoal	Backup	in Liters	mg/cu m
ND	ND	199	ND	328	0.607
ND	ND	191	ND	327	0.584
ND	ND	246	ND	387	0.636
ND	ND	248	ND	396	0.626
ND	ND	291	ND	464	0.627
ND	ND	297	ND	470	0.632

ND = Not detectable; the detection limit is 2 µg in a total volume of 10 ml (0.2 µg/ml as TeF_6).

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TABLE 2

Data Sheet: Tellurium Hexafluoride, S187
(Lot 105 Charcoal/100 mg, Samples Stored 1 Day)

Analysis

Level	0.5S		1S			2S		
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
38.0	36.2	0.953	75.9	71.4	0.941	151.8	144.3	0.951
38.0	36.4	0.958	75.9	63.0*	0.830*	151.8	138.8	0.914
38.0	35.8	0.942	75.9	70.6	0.930	151.8	144.6	0.953
38.0	36.2	0.953	75.9	70.8	0.933	151.8	144.6	0.953
38.0	36.7	0.966	75.9	72.0	0.949	151.8	145.2	0.957
38.0	36.7	0.966	75.9	71.4	0.941	151.8	144.3	0.951
n =		6			5			6
mean		0.956			0.939			0.947
std dev		0.0091			0.0075			0.0161
CV_1		0.0096			0.0080			0.0170

$\overline{CV_1}$ 0.0124

$\overline{CV_{A+\overline{DE}}}$ 0.0134

*These values excluded from statistical analysis based on Grubb's test for outliers.

TABLE 3

Data Sheet: Tellurium Hexafluoride, S187
(Lot 105/100 mg, Samples Stored 5 Days)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
38.4	34.6	0.901	76.8	67.2	0.875	153.6	133.9	0.872
38.4	31.6	0.823	76.8	67.2	0.875	153.6	142.0	0.924
38.4	33.1	0.862	76.8	62.5	0.814	153.6	137.3	0.894
38.4	32.2	0.839	76.8	67.6	0.880	153.6	137.3	0.894
38.4	32.6	0.849	76.8	74.8	0.974	153.6	141.0	0.918
38.4	33.1	0.862	76.8	66.3	0.863	153.6	135.0	0.879
n =		6			6			6
mean		0.856			0.880			0.897
std dev		0.0265			0.0520			0.0207
CV_1		0.0310			0.0591			0.0230

$\overline{CV}_1$ 0.0408

$\overline{CV}_{A+\overline{DE}}$ 0.0440

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and temperature correction factors have been used to determine µg added for each case, it is highly probable that the observed difference could have been due to differences in the absolute concentration of the gas stock standards.

To resolve the stability issue, a full set of 18 "generated" samples was collected using the vapor generator and dilution system charged with controlled amounts of tellurium hexafluoride. The backup sections were removed immediately after sampling to prevent any sample migration and 9 samples, 3 at each test level, were analyzed after an overnight period; the other 9 samples were analyzed after storage at room temperature for 7 days. The "µg found" shown in Table 4 have not been corrected for any desorption efficiency value and clearly show that the samples are stable over the 7-day storage at room temperature.

On the basis of these data the desorption efficiency curve used for subsequent calculations was based on the pooled data derived from the two sets of spiked samples because the observed differences in the DE values for the 1- and 5-day-old spiked samples may be simply due to experimental variations in sample handling and the preparation of the gas stock standards.

Generation

Test atmosphere samples at the concentration level equivalent to 0.5, 1 and 2X OSHA standard were generated by delivering tellurium hexafluoride gas in a gas tight syringe using the syringe injector delivery system and vapor dilution arrangement described in the Butyl Acetate S47 Backup Data Report and Attachment. An independent estimate of the generator concentration at this low level could not be obtained because no other collection medium or analytical method was found to be better than the sampling and analytical method used for validation. Measurements based on syringe delivery rate were also found to be grossly inadequate because of the errors associated in measuring the slow delivery rate (4 µl/min) required to produce the 2S test level when the main line air flow is maintained at 0.100 cu m/min. Since collection efficiency was found to be 100%, the best estimate of generator concentration was based on the tellurium hexafluoride found in the collected samples, properly corrected for desorption efficiency.

Three sets of 18 generated samples were collected and analyzed as described previously. In each case, the dilution ratios were maintained at 0.233, 0.486 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. The data for these experimental studies are summarized in Table 5--for two full sets of 18 samples stored for 1 day and for 7 days-- and in Table 6--for the set of 18 samples stored and analyzed such that the first three samples at each test level represent 1-day-old samples while the rest were 7-day-old samples. For each set, the dilution ratios calculated based on the

TABLE 4

Stability of Tellurium Hexafluoride
Collected on Lot 105 Charcoal/100 mg

Sample Volume Collected: 390 Liters

Test Level		µg Found	
		Stored 1 Day	Stored 7 Days
0.5		33.1	34.1
		32.8	34.1
		32.2	32.6
	Mean =	32.7	33.6
1S		41.6*	61.0
		62.5	59.6
		61.5	61.5
	Mean =	62.0	60.7
2S		137.3	133.9
		134.4	136.3
		134.4	135.4
	Mean =	135.4	135.2

*** This value excluded from statistical analysis.**

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TABLE 5

Data Sheet: Tellurium Hexafluoride, S187
(Lot 105 Charcoal/100 mg)

Samples Stored 1 Day			Samples Stored 7 Days		
	Found			Found	
Corr µgΔ	Liters	mg/cu m	Corr µgΔ	Liters	mg/cu m
29.1	408	0.0713	60.4	393	0.1537
28.3	406	0.0697	59.5	390	0.1526
27.0	408	0.0662	59.3	391	0.1517
29.8	406	0.0734	59.7	390	0.1531
29.3	411	0.0713	59.9	394	0.1520
29.6	411	0.0720	59.3	395	0.1501
	n = 6			n = 6	
	mean	0.0707		mean	0.1522
	std dev	0.00249		std dev	0.00126
	CV_2	0.0352		CV_2	0.00827
40.4	397	0.1018*	87.7	382	0.230*
59.9	418	0.1433	124.4	401	0.310
58.9	405	0.1454	119.9	389	0.308
59.7	408	0.1463	122.4	392	0.312
59.1	409	0.1445	122.8	393	0.312
59.5	408	0.1458	123.5	392	0.315
	n = 5			n = 5	
	mean	0.1451		mean	0.311
	std dev	0.00118		std dev	0.00261
	CV_2	0.00816		CV_2	0.00838
122.5	410	0.2988	253.2	394	0.643
117.7	408	0.2886	251.0	392	0.640
115.7	403	0.2871	253.7	387	0.656
117.1	412	0.2842	252.7	396	0.638
118.1	404	0.2923	253.4	388	0.653
120.6	410	0.2941	254.7	394	0.646
	n = 6			n = 6	
	mean	0.2909		mean	0.646
	std dev	0.00528		std dev	0.00718
	CV_2	0.01814		CV_2	0.01112
	$\overline{CV}_2$	0.0241		$\overline{CV}_2$	0.0094

ΔCorrected for DE factor
*These values excluded from statistical analysis

TABLE 6

Data Sheet: Tellurium Hexafluoride, S187
(Samples Stored 1 and 7 Days)

Sampling and Analysis

Test Level	Found			
	µg	Corr µgΔ	Liters	mg/cu m
0.5S	33.1	36.8	391	0.0941
	32.8	36.4	388	0.0938
	32.2	35.8	390	0.0918
	34.1	37.9	388	0.0977
	34.1	37.9	393	0.0964
	32.6	36.2	394	0.0919
			n = 6	
			mean	0.0943
			std dev	0.00238
			CV_2	0.0252
1S	41.6*	45.7	381	0.1199*
	62.5	68.7	400	0.1718
	61.5	67.6	388	0.1742
	61.0	67.0	391	0.1714
	59.6	65.5	392	0.1671
	61.5	67.6	391	0.1729
			n = 5	
			mean	0.1715
			std dev	0.00268
			CV_2	0.0156
2S	137.3	147.6	393	0.376
	134.4	144.5	391	0.370
	134.4	144.5	386	0.374
	133.9	144.0	394	0.365
	136.3	146.6	387	0.379
	135.4	145.6	392	0.371
			n = 6	
			mean	0.373
			std dev	0.00493
			CV_2	0.0132
			$\overline{CV}_2$	0.0189

ΔCorrected for DE factor
*These values excluded from statistical analysis

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mg/cu m found at each test level agree closely with the measured dilution ratios noted above. The calculated dilution ratios and atmospheric temperature and pressure for these samples are shown below.

Sample Description	Dilution Ratio	°C, mm Hg
1 Day Old	0.243, 0.499, 1.000	21°, 756
7 Days Old	0.236, 0.481, 1.000	21°, 756
1 and 7 Days	0.246, 0.460, 1.000	23°, 761

Breakthrough

The first section of the charcoal tube was found to hold at least 290 micrograms of tellurium hexafluoride when a test atmosphere containing 0.63 mg/cu m was sampled at 1.1 liters per minute for 420 minutes; (see Table 1) i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent. Additional collection efficiency data are shown in Table 7 when a test atmosphere containing 0.64 mg/cu m was sampled at 1.1 liters per minute. The collection efficiency found was 100%.

Precision and Accuracy

The statistical procedures used are described in Reference 1. The data used for the statistical calculations are shown in Tables 2 and 6 for the analytical and generated samples respectively.

$\overline{CV}_1 = 0.0124$ $\overline{CV}_2 = 0.0189$ $\overline{CV}_T = 0.0537$

$\overline{CV}_T$ is a measure of accuracy because the collection efficiency has been established to be 100% and any analytical bias is accounted for by using the appropriate DE correction factor.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 7

Collection Efficiency: Tellurium Hexafluoride, S187
Lot 105 Charcoal/100 mg, 400 Liters at 1.1 Liters per Minute

µg Found			
Front	Backup	Total	% Collected in Front
255	ND	255	100
251	ND	251	100
255	ND	255	100
254	ND	254	100
255	ND	255	100
256	ND	256	100

Average Collection Efficiency 100%

ND = Not detectable; the detection limit is 2 µg in a total volume of 10 ml (0.2 µg/ml as tellurium hexafluoride equivalent to 0.1 µg/ml as tellurium).

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Backup Data Report

Substance: Rhodium, Metal Fume and Dust, No. S188

OSHA Standard: 0.1 mg/cu m

Chemical Used for Validation: Rhodium Nitrate, $Rh(NO_3)_3.2H_2O$, Ventron Alfa Products

Procedure

The general procedure used is described in NIOSH Method No. S188 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 720-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of an aqueous solution of the analyte was added to 37 mm Type AA Millipore filters. The sample-containing filters were digested with concentrated nitric acid and the analyte solubilized with hydrochloric acid. Analyses were done with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The absorbance, measured at 343.5 nm, was used as a measure of the rhodium concentration in the sample. Appropriate standard solutions were analyzed on the same day the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S188.

Modification

P&CAM 173 was modified by recommending the addition of a solution of potassium bisulfate in order to eliminate the interferences of other common cations and also anions like nitrates and phosphates.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of rhodium nitrate containing 1.27 g/liter as rhodium into a dry, solvent-free air stream flow. The atomizer flowrate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 480 minutes (720 liters). Since collection efficiency was found to be 1.00 ± 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

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Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate rhodium was determined by collecting six filter samples at an air sample concentration of 0.21 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency was 100% when a test atmosphere containing 0.21 mg/cu m was sampled for 480 minutes. (Table 1).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0217$ $\overline{CV}_2 = 0.0609$ $\overline{CV}_T = 0.079$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

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Table 1

Collection Efficiency: Rhodium, Metal Fume and Dust
(1.5 liter per minute for 480 minutes)

Test Concentration: Estimated to be 0.21 mg/cu m

µg Found in			% Found
Front	Backup	Total	In Front
136	0	136	100
177	0	177	100
162	0	162	100
147	0	147	100
155	0	155	100
155	0	155	100

Average Collection Efficiency 100%

Data Sheet: Rhodium, Metal Fume and Dust, S188

Analysis

Level

µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
36.0	33.8	0.939	72.0	69.5	0.965	144.0	138.8	0.964
36.0	33.8	0.939	72.0	70.2	0.975	144.0	137.0	0.951
36.0	33.8	0.939	72.0	70.2	0.975	144.0	136.3	0.947
36.0	32.0	0.889	72.0	71.2	0.989	144.0	140.3	0.974
36.0	31.2	0.867	72.0	69.5	0.965	144.0	135.8	0.943
36.0	33.2	0.922	72.0	69.0	0.958	144.0	137.0	0.951
n =		6			6			6
mean		0.916			0.971			0.955
std dev		0.0308			0.0109			0.0117
CV_1		0.0337			0.0113			0.0122

$\overline{CV}_1$ 0.0217

$\overline{CV}_{A+\overline{CE}}$ 0.0234

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Data Sheet: Rhodium, Metal Fume and Dust, S188
Sampling and Analysis

Test Level	µg	Liters	µg/ℓ or mg/cu m
0.5S	45.0	735	0.0612
	40.0	734	0.0545
	43.8	730	0.0600
	40.8	734	0.0556
	41.2	732	0.0563
	41.2	738	0.0558
		n = 6	
		mean	0.0572
		std dev	0.0027
		CV_2	0.0472
1S	95.0	736	0.1291
	91.2	737	0.1237
	91.2	733	0.1244
	90.5	739	0.1225
	88.2	742	0.1189
	87.0	738	0.1179
		n = 6	
		mean	0.1228
		std dev	0.0041
		CV_2	0.0330
2S	136.3	736	0.1852
	176.5	735	0.2401
	162.0	735	0.2204
	147.0	735	0.2000
	155.0	733	0.2115
	155.0	748	0.2072
		n = 6	
		mean	0.2107
		std dev	0.0186
		CV_2	0.0884
		$\overline{CV_2}$	0.0609

Backup Data Report

Substance: Rhodium, Soluble Salts, No. S189

OSHA Standard: 0.001 mg/cu m

Chemical Used for Validation: Rhodium Nitrate, $Rh(NO_3)_3 \cdot 2H_2O$, Ventron Alfa Products

Procedure

The general procedure used is described in NIOSH Method No. S189 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 370-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of an aqueous solution of the analyte was added to 37 mm Type AA Millipore filters. The sample-containing filters were digested with concentrated nitric acid followed by nitric/perchloric acid mixture.

The samples were analyzed in a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 503, equipped with a heated graphite atomizer HGA Model 2100, and a Deuterium Background Corrector. A Hewlett Packard Recorder, Model 17501A was used. The source was an Electrodeless Discharge Lamp powered by a Perkin-Elmer EDL power supply. The rhodium absorption line at 369.5 nm was used for the assay.

With the aid of an Eppendorf automatic pipettor with disposable plastic tips, duplicate 50-microliter aliquots of the desorbed sample solutions were injected directly into selected graphite tubes. Argon was used as the inert gas stream flowing through the furnace. The furnace conditions were as follows:

Sample Cycle	Time in Seconds	Temperature, °C
Sample drying	40	150
Sample charring	20	500
Sample atomization	10	2700

Peak areas of the absorption peaks as determined using the Perkin-Elmer 503 integrator accessory were used to determine the quantity of rhodium present in the sample. The analyses were carried out such that the sample solutions were carefully alternated with solutions of calibration standards of about the same response as the sample in order to minimize errors due to observed instrument response variations. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S189.

Modification

P&CAM 173 was modified by recommending the perchloric acid digestion and the use of a high-temperature graphite atomizer. Leaching with hot water is not satisfactory because low recoveries are obtained, 14-30% over the concentration range of 0.5 to 2 X OSHA standard. A similar low recovery had been observed in the case of platinum soluble salts, S191 Backup Data Report.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of rhodium nitrate containing 0.013 g/liter as rhodium into a dry, solvent-free air stream flow. The atomizer flowrate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 240 minutes (370 liters). Since collection efficiency was found to be 99.6 ± 0.9%, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate rhodium was determined by collecting six filter samples at an air sample concentration of ca. 0.0030 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency was 99.6% when a test atmosphere containing 0.0030 mg/cu m was sampled for 240 minutes. (Table 1).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0699 \qquad \overline{CV}_2 = 0.0385 \qquad \overline{CV}_T = 0.0694$$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Collection Efficiency: Rhodium, Soluble Salts

μg Found			
Front	Backup	Total	% Collected in Front
1.125	0.000	1.125	100.0
1.100	0.000	1.100	100.0
1.125	0.000	1.125	100.0
1.100	0.000	1.100	100.0
1.075	0.025	1.100	97.7
1.125	0.000	1.125	100.0

Average Collection Efficiency 99.6 ± 0.9%

Data Sheet: Rhodium, Soluble Salts S189

Analysis

Level	0.5S			1S			2S		
	µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
	0.170	0.205	1.206	0.340	0.350	1.029	0.680	0.693	1.019
	0.170	0.178	1.047	0.340	0.359	1.056	0.680	0.708	1.041
	0.170	0.197	1.159	0.340	0.345	1.015	0.680	0.731	1.075
	0.170	0.171	1.006	0.340	0.341	1.003	0.680	0.718	1.056
	0.170	0.192	1.129	0.340	0.330	0.971	0.680	0.663	0.975
	0.170	0.163	0.959	0.340	0.403	1.185	0.680	0.660	0.971
	n =		6			6			6
	mean		1.084			1.043			1.023
	std dev		0.0955			0.0750			0.0428
	CV_1		0.0881			0.0719			0.0418

$\overline{CV}_1$ 0.0699

$\overline{CV}_{A+\overline{CE}}$ 0.0756

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Data Sheet: Rhodium, Soluble Salts S189

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	0.145	365	0.000397
	0.155	364	0.000426
	0.150	363	0.000413
	0.143	365	0.000392
	0.145	364	0.000398
	0.143	367	0.000390
		n = 6	
		mean	0.000403
		std dev	0.000014
		CV_2	0.0347
1S	0.290	366	0.000792
	0.283	366	0.000773
	0.313	364	0.000860
	0.300	367	0.000817
	0.315	369	0.000854
	0.315	367	0.000858
		n = 6	
		mean	0.000826
		std dev	0.000037
		CV_2	0.0453
2S	0.630	366	0.001721
	0.653	365	0.001789
	0.687	365	0.001882
	0.660	365	0.001808
	0.637	365	0.001745
	0.690	372	0.001855
		n = 6	
		mean	0.001800
		std dev	0.000062
		CV_2	0.0344
		$\overline{CV_2}$	0.0385

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Backup Data Report

Substance: Selenium Compounds (as Se), No. S190

OSHA Standard: 0.2 mg/cu m

Chemical Used for Validation: Potassium Selenite, K_2SeO_3, Atomergic Chemetals, 99%

Procedure

The general procedure used is described in NIOSH Method No. S190 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 360-liter sample at 0.5, 1 and 2 times the OSHA standard. The analytical samples were prepared by adding aliquots of an aqueous solution of potassium selenite containing amounts of selenium equivalent to that present in a 360-liter sample at 0.5, 1 and 2X OSHA standard. 37-mm Type AA Millipore filters were used for these studies. The samples were extracted from the filters with 0.1 N nitric acid. Analyses were done with a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer with a deuterium background corrector. The absorbance, measured at 196.0 nm, was used as a measure of the selenium concentration in the sample. Appropriate standard solutions were analyzed on the same day the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S190.

Modification

The acid digestion route adapted in P&CAM 173 as a general route to recovery of metals from cellulose membrane filters did not work well for selenium based on data obtained from filters spiked with an aqueous solution of potassium selenite. Digestion using either nitric acid or nitric acid/perchloric acid gave equally low recoveries (80%) with good precision (CV = 0.06). Tests also indicate that the low recoveries were not due to interferences caused by the "digestion liquor" because a set of 18 spiked samples digested with nitric acid and analyzed using the standard addition method also gave low recoveries. The comparative data using nitric acid digestion and analysis by either the external standard method or the standard addition method gave low recoveries, as shown in Tables 1 and 2. The average recoveries obtained by these methods, which were respectively 79% and 81%, indicated that the losses are probably due to volatilization during the digestion process.

An alternate route using extraction with dilute acid was subsequently explored. The rationale behind the approach is based on the fact that several of the selenium compounds including selenium metal are

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reported to be acid soluble. The acid extraction route tested proved to be adequate yielding an average recovery of 92% for 18 Type AA Millipore filters spiked with an aqueous solution of potassium selenite containing selenium equivalent to that present in a 360-liter sample for 0.5, 1 and 2X OSHA standard. The data are summarized in Table 3.

It should be noted that the applicability of this method is limited to the selenium compounds soluble in acid. Thus a bulk sample must always be brought back to the laboratory in order to determine the solubility in acid as well as the recovery of the selenium from filters spiked with known amounts of the bulk samples when the acid extraction procedure is used.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of potassium selenite containing 2.3 g/liter as selenium into a dry, solvent-free air stream flow. The atomizer flow rate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the main-line, then twofold and fourfold dilutions made to obtain the 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 240 minutes (360 liters). Details of the sample generation/dilution system and collection equipment may be found in the Octachloro-naphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate selenium compounds was determined by collecting six filter samples at an air sample concentration of 0.50 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency found was 100% when a test atmosphere containing 0.50 mg/cu m was sampled for 240 minutes (Table 4).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0401$ $\overline{CV}_2 = 0.0735$ $\overline{CV}_T = 0.0904$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Table 1

Data Sheet: Selenium Compounds as Se, S190
(Digestion with Nitric Acid, External Standard Method)

Analysis

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
34.3	27.0	0.787	68.5	55.5	0.810	137.0	111.3	0.812
34.3	26.0	0.758	68.5	52.8	0.771	137.0	117.3	0.856
34.3	29.3	0.854	68.5	53.3	0.778	137.0	95.3	0.696
34.3	28.3	0.825	68.5	54.5	0.796	137.0	110.8	0.809
34.3	27.8	0.810	68.5	53.8	0.785	137.0	99.5	0.726
34.3	26.5	0.773	68.5	53.3	0.778	137.0	111.8	0.816
n =		6			6			6
mean		0.801			0.786			0.786
std dev		0.0355			0.0143			0.0612
CV_1		0.0443			0.0183			0.0778

$\overline{CV}_1$ 0.0528

$\overline{CV}_{A+\overline{DE}}$ 0.0570

Table 2

Data Sheet: Selenium Compounds as Se, S190
(Digestion with Nitric Acid, Standard Addition Method)

Analysis

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
34.3	29.8	0.869	68.5	57.8	0.844	137.0	121.4	0.886
34.3	29.8	0.869	68.5	60.5	0.883	137.0	102.8	0.750
34.3	26.8	0.781	68.5	51.0	0.745	137.0	121.4	0.886
34.3	*	*	68.5	49.6	0.724	137.0	118.3	0.864
34.3	26.8	0.781	68.5	50.2	0.733	137.0	118.3	0.864
34.3	25.9	0.755	68.5	48.1	0.702	137.0	121.4	0.886
n =		5			6			6
mean		0.811			0.772			0.856
std dev		0.0540			0.0734			0.0530
CV_1		0.0666			0.0951			0.0620

$\overline{CV}_1$ 0.0766

$\overline{CV}_{A+\overline{DE}}$ 0.0828

*Samples lost

Table 3

Data Sheet: Selenium Compounds as Se, S190
(Extraction with 0.1 N Nitric Acid)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
35.9	28.3	0.788	71.9	66.7	0.928	143.7	131.7	0.916
35.9	30.3	0.844	71.9	68.3	0.950	143.7	136.7	0.951
35.9	32.7	0.911	71.9	68.5	0.953	143.7	132.0	0.919
35.9	32.3	0.900	71.9	72.7	1.011	143.7	132.7	0.923
35.9	33.3	0.928	71.9	68.0	0.946	143.7	128.0	0.891
35.9	32.0	0.891	71.9	69.0	0.960	143.7	134.0	0.932
n =		6			6			6
mean		0.877			0.958			0.922
std dev		0.0519			0.0281			0.0197
CV_1		0.0592			0.0293			0.0214

$\overline{CV}_1$ 0.0401

$\overline{CV}_{A+\overline{DE}}$ 0.0433

Table 4

Collection Efficiency: Selenium Compounds as Se, S190
(Extraction with 0.1 N Nitric Acid)

μg Found			
Front	Backup	Total	% Collected in Front
168.5	ND	168.5	100
117.2	ND	117.2	100
169.5	ND	169.5	100
171.5	ND	171.5	100
157.5	ND	157.5	100
172.5	ND	172.5	100

Average Collection Efficiency 100%

ND = Not detectable; the lower limit of detection is 3 μg in a total volume of 25 ml.

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Table 5

Data Sheet: Selenium Compounds as Se, S190
(Extraction with 0.1 N Nitric Acid)

Sampling and Analysis

Test Level	Found			
	µg	Corr µg	Liters	µg/ℓ or mg/cu m
0.5S	31.2	33.9	362	0.0936
	29.2	31.7	360	0.0881
	33.2	36.1	359	0.1006
	37.2	40.4	361	0.1119
	37.2	40.4	360	0.1122
	32.2	35.0	363	0.0964
			n = 6	
			mean	0.1005
			std dev	0.0098
			CV_2	0.0976
1S	69.2	75.2	362	0.2077
	74.2	80.7	363	0.2223
	80.2	87.2	361	0.2416
	83.2	90.4	364	0.2484
	72.2	78.5	365	0.2151
	75.2	81.7	363	0.2251
			n = 6	
			mean	0.2267
			std dev	0.0156
			CV_2	0.0686
2S	168.5	183.2	362	0.506
	117.2	127.4	362	0.352*
	169.5	184.2	362	0.509
	171.5	186.4	362	0.515
	157.5	171.2	361	0.474
	172.5	187.5	365	0.514
			n = 5	
			mean	0.504
			std dev	0.0169
			CV_2	0.0336
			$\overline{CV_2}$	0.0735

*This value excluded based on Grubb's test.

Backup Data Report

Substance: Platinum, Soluble Salts, No. S191

OSHA Standard: 0.002 mg/cu m

Chemical Used for Validation: Potassium Chloroplatinate, K_2PtCl_6, (99.9%), Ventron Alfa Products

Procedure

The general procedure used is described in NIOSH Method No. S191 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectrophotometry. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 730-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of an aqueous solution of the analyte was added to 37-mm Type AA Millipore filters. The sample-containing filters were digested with concentrated nitric acid followed by nitric/perchloric acid mixture.

The samples were analyzed in a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 503, equipped with a heated graphite atomizer, HGA Model 2100, and a deuterium background corrector. A Hewlett Packard Recorder, Model 17501A was used. The source was an Electrodeless Discharge Lamp powered by a Perkin-Elmer EDL power supply. The platinum absorption line at 265.9 nm was used for the assay.

With the aid of an Eppendorf automatic pipettor with disposable plastic tips, duplicate 50-microliter aliquots of the desorbed sample solutions were injected directly into selected graphite tubes. Argon was used as the inert gas stream flowing through the furnace. The furnace conditions were as follows:

Sample Cycle	Time in Seconds	Temperature, °C
Sample drying	40	150
Sample charring	20	500
Sample atomization	10	2700

Peak areas of the absorption peaks as determined using the Perkin-Elmer 503 integrator accessory were used to determine the quantity of platinum present in the sample. The analyses were carried out such that the sample solutions were carefully alternated with solutions of calibration standards of about the same response as the sample in order to minimize errors due to observed instrument response variations. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S191.

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Modification

P&CAM 173 was modified by recommending the perchloric acid digestion and the use of a high-temperature graphite atomizer. Leaching with hot water is not satisfactory because low recoveries are obtained, 22-60% over the concentration range of 0.5 to 2X OSHA standard. A similar low recovery trend was observed in the case of rhodium soluble salts, S189 Backup Data Report.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of potassium chloroplatinate containing 0.018 g/liter as platinum into a dry, solvent-free air stream flow. The atomizer flow rate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 480 minutes (720 liters). Since collection efficiency was found to be 99.7 $\pm$ 0.6%, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate platinum was determined by collecting six filter samples at an air sample concentration of ca. 0.0031 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency was 99.7% when a test atmosphere containing 0.0031 mg/cu m was sampled for 480 minutes. (Table 1)

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0352$ $\overline{CV}_2 = 0.0345$ $\overline{CV}_T = 0.0624$

Reference

Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Table 1

Collection Efficiency: Platinum, Soluble Salts

µg Found			
Front	Backup	Total	% Collected in front
2.218	0.000	2.218	100.0
2.230	0.000	2.230	100.0
2.323	0.030	2.353	98.7
2.335	0.000	2.335	100.0
2.125	0.000	2.125	100.0
1.338*	0.000	1.338	*

Average Collection Efficiency...99.7 $\pm$ 0.6%

*Excluded from statistical analysis based on Grubbs' test for outlying results.

Data Sheet: Platinum, Soluble Salts, S191

Analysis

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
0.730	0.735	1.007	1.460	1.485	1.017	2.920	2.887	0.989
0.730	0.747	1.023	1.460	1.424	0.975	2.920	2.695	0.923
0.730	0.701	0.960	1.460	1.435	0.983	2.920	2.659	0.911
0.730	0.740	1.014	1.460	1.373	0.940	2.920	2.931	1.004
0.730	0.711	0.974	1.460	1.395	0.955	2.920	2.824	0.967
0.730	0.696	0.953	1.460	1.339	0.917	2.920	2.856	0.978
n =		6			6			6
mean		0.989			0.965			0.962
std dev		0.0299			0.0351			0.0371
CV_1		0.0302			0.0364			0.0386

$\overline{CV}_1$ 0.0352

$\overline{CV}_A + \overline{CE}$ 0.0381

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Data Sheet: Platinum, Soluble Salts, S191

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	0.602	728	0.000827
	0.560	725	0.000772
	0.560	722	0.000776
	0.550	727	0.000757
	0.560	724	0.000773
	0.613	731	0.000839
		n = 6	
		mean	0.000791
		std dev	0.0000337
		CV_2	0.0426
1S	0.865*	729	0.001187*
	1.170	730	0.001603
	1.190	726	0.001639
	1.170	732	0.001598
	1.180	735	0.001605
	1.147	731	0.001569
		n = 5	
		mean	0.001603
		std dev	0.0000249
		CV_2	0.01554
2S	2.218	729	0.00304
	2.230	728	0.00306
	2.323	728	0.00319
	2.335	728	0.00321
	2.125	726	0.00293
	1.338*	740	0.00181*
		n = 5	
		mean	0.00309
		std dev	0.000115
		CV_2	0.0374
		$\overline{CV}_2$	0.0345

*These values excluded from statistical analysis based on Grubbs' test for outlying results.

Backup Data Report

Substance: Molybdenum, Soluble Compounds, No. S193

OSHA Standard: 5 mg/cu m

Chemical used for Validation: Sodium Molybdate, Fisher Scientific Co., certified

Procedure:

The general procedure used is described in NIOSH Method No. S193 which is a modification of P&CAM 173 for filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equal to that present in a 90-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in water was added to 37 mm Type AA Millipore filters. The analyte was leached from the filter with hot water and analyzed with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The absorbance, measured at 313.3 nm, was used as a measure of molybdenum concentration in the sample. Appropriate standard solutions were analyzed alternately with samples to minimize observed variations in flame responses during any given day. Similarly, the 18 generated samples (6 at each of the 0.5, 1 and 2X OSHA standard levels) were analyzed accordingly. Details of the extraction and analytical procedures may be found in Section 8.3 of NIOSH Method No. S193.

Modification

P&CAM 173 was modified in that leaching with hot water is recommended instead of the acid digestion route. This leaching process was found to give good recovery (100%) of a soluble molybdenum compound, sodium molybdate. The analysis procedure was also modified such that a calibration curve is not used, instead samples are analyzed alternately with standards. This procedure is necessary because it has been observed that there is a marked decrease in the slope of the calibration curve obtained at the beginning of the day as compared to subsequent calibration runs. These variations are believed to be due to carbon buildup at the burner head.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous sodium molybdate solution containing 56.1 g/liter as molybdenum into a dry, solvent-free air stream flow. The atomizer flowrate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5 times the OSHA standard

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level. All 6 samples at the three test levels were collected simultaneously at 1.5 liters per minute for 60 minutes (90 liters). Since collection efficiency was found to be 1.00 $\pm$ 0.01, the concentration in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate soluble molybdenum compounds was determined by collecting six filter samples at air sample concentrations of 5.6 and 9.1 mg/cu m. The physical layout of the filter series (front and backup) used for each of the two sets of six samples collected was such that the two filters were mounted back to back in contact with each other and supported by the backup pad. The average collection efficiency found was 99.6% for the 9.1 mg/cu m series and 100% for the 5.6 mg/cu m series. (Table 1.)

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for soluble molybdenum compounds using the equation shown in Reference 2.

The sampling and analysis data gave a chi squared value of 10.6 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for molybdenum, however, still show good precision and pooling will not introduce significant error. For this reason CV_T is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0389$ $\overline{CV}_2 = 0.0722$ $\overline{CV}_T = 0.089$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

TABLE 1

Collection Efficiency: Molybdenum, Soluble Compounds
(Sodium Molybdate)

Test Concentration mg/cu m	µg Found on Filter			% Found
	Front	Backup	Total	in front
5.6	507	0	507	100
	509	0	509	100
	462	0	462	100
	523	0	523	100
	521	0	521	100
	508	0	508	100
	Average Collection Efficiency			100 ±0%
9.1	748	53	801	93.4*
	833	0	833	100
	788	0	788	100
	865	0	865	100
	875	0	875	100
	838	15	853	98.2
	Average Collection Efficiency			99.6 ±0.8%

*This value excluded from statistical analysis based on Grubbs' Outlier test.

Data Sheet: Molybdenum Soluble Compounds, S193

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
237.0	230.0	0.971	475	468	0.985	950	1015	1.068
237.0	242.5	1.023	475	495	1.042	950	1018	1.072
237.0	247.5	1.044	475	468	0.985	950	1015	1.068
237.0	220.0	0.928	475	440	0.926	950	993	1.045
237.0	222.5	0.939	475	443	0.933	950	1022	1.076
237.0	222.5	0.939	475	458	0.964	950	1028	1.082
n =		6			6			6
mean		0.974			0.973			1.069
std dev		0.0487			0.0423			0.0127
CV_1		0.0500			0.0435			0.0119

$\overline{CV_1}$ 0.0389

$\overline{CV_{A+CE}}$ 0.0420

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Data Sheet: Molybdenum Soluble Compounds, S193

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m
0.5S	142.0	91.5	1.552
	194.3	91.2	2.131
	189.8	90.9	2.088
	174.8	91.4	1.912
	177.8	91.1	1.952
	196.5	91.9	2.138
		n = 6	
		mean	1.962
		std dev	0.2218
		CV_2	0.1131
1S	389	91.7	4.24
	394	91.8	4.29
	389	91.3	4.26
	372	92.0	4.04
	393	92.4	4.25
	393	91.9	4.28
		n = 6	
		mean	4.23
		std dev	0.0933
		CV_2	0.0221
2S	839	91.7	9.15
	929	91.5	10.15
	930	91.6	10.15
	901	91.5	9.85
	916	91.4	10.02
	852	93.1	9.15
		n = 6	
		mean	9.75
		std dev	0.474
		CV_2	0.0486
		$\overline{CV}_2$	0.0722

Backup Data Report

Substance:	Barium, Soluble Compounds, S198
OSHA Standard:	0.5 mg/cu m
Chemical Used for Validation:	Barium Chloride Dihydrate (Bakers Analyzed Reagent) Solutions used for validation were standardized by precipitating and weighing barium as the sulfate.

Procedure

The general procedure is described in NIOSH Method No. S198 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations representing 168-liter air samples at 0.5, 1.0, and 2.0 times the OSHA standard. The appropriate aliquot of an aqueous solution of the analyte was added to 37-mm / 0.8 micron Type AA Millipore filters. The soluble barium compounds were leached from the filter with hot distilled water and dissolved in dilute hydrochloric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer. The absorbance, measured at 553.6 nm, was used as a measure of the barium concentration in the sample. A similar procedure was used for the analysis of 18 generated samples, 6 each at approximately 0.5, 1, and 2 times the OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S198.

Modification

P&CAM 173 was modified by use of a hot water leach to remove soluble barium compounds from the filter material.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the Nickel report (Reference No. 1). Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing aqueous solutions of barium chloride at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of about 1.4 liter per minute for 120 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate soluble barium compounds was determined by collecting

eight filter samples at an air sample concentration of 1.1 mg/cu m (2X OSHA standard level). The physical arrangement of the filters was such that backup filters were mounted in contact with each collecting filter and both supported by the support pad. The collection efficiency was 1.00 when the test atmosphere was sampled for 120 minutes. Therefore, no correction for collection efficiency is necessary.

Collection Efficiency

Front Filter Found µg	Backup Filter Found µg	Collection Efficiency
184.5	N.D.	1.00
181.5	N.D.	1.00
182.5	N.D.	1.00
185.0	N.D.	1.00
179.0	N.D.	1.00
180.0	N.D.	1.00
179.0	N.D.	1.00
182.0	N.D.	1.00

N.D. = Not Detected (< 1.00 µg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.025 \qquad \overline{CV}_2 = 0.018 \qquad \overline{CV}_T = 0.054$

Data Sheet: Barium, Soluble Compounds S198

Analysis

Level	0.5S		1S			2S		
µg added	µg found	A.M.R.	µg added	µg found	A.M.R.	µg added	µg found	A.M.R.
43.5	45.0	1.034	88.5	88.8	1.003	177.0	178.8	1.010
43.5	43.6	1.002	88.5	88.8	1.003	177.0	183.8	1.038
43.5	46.3	1.064	88.5	88.3	0.998	177.0	182.5	1.031
43.5	45.0	1.034	88.5	91.3	1.032	177.0	171.3	0.968
43.5	43.6	1.002	88.5	87.5	0.989	177.0	174.5	0.986
43.5	46.3	1.064	88.5	88.8	1.003	177.0	185.0	1.045
n =		6			6			6
mean		1.033			1.005			1.013
std dev		0.028			0.014			0.031
CV_1		0.027			0.014			0.031

$\overline{CV}_1$ 0.025

$\overline{CV}_{A+\overline{AMR}}$ 0.027

Based on the above results, no analytical method recovery (A.M.R.) correction is necessary.

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Data Sheet: Barium, Soluble Compounds S198

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.0475	168.6	0.2817
	0.0456	168.0	0.2714
	0.0480	168.0	0.2857
	0.0475	168.0	0.2827
	0.0463	167.4	0.2766
	0.0487	168.0	0.2899
		n = 6	
		mean	0.2813
		std dev	0.0066
		CV_2	0.023
1S	0.0925	168.6	0.549
	0.0918	168.0	0.546
	0.0906	168.0	0.539
	0.0895	168.0	0.533
	0.0925	167.4	0.553
	0.0938	168.0	0.558
		n = 6	
		mean	0.546
		std dev	0.009
		CV_2	0.016
2S	0.1845	168.6	1.094
	0.1815	168.0	1.080
	0.1825	168.0	1.086
	0.1850	168.0	1.101
	0.1790	167.4	1.069
	0.1800	168.0	1.071
		n = 6	
		mean	1.084
		std dev	0.013
$\overline{CV}_2$ 0.018		CV_2	0.012

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, Nickel, No. S206, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Yttrium, No. S200
OSHA Standard:	1 mg/cu m
Chemical Used for Validation:	Yttrium metal (Johnson-Matthey) Solutions used for validation were standardized by EDTA titration

Procedure

The general procedure is described in NIOSH Method No. S200 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations representing 500-liter samples at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in dilute hydrochloric acid and nitric acid was added to 37-mm, 0.8-micron Type AA Millipore filters. The filters containing the samples were digested with concentrated nitric and perchloric acids. The analyte was dissolved in dilute hydrochloric acid. Analyses were done with a Perkin-Elmer Model 305B atomic absorption spectrophotometer. The absorbance, measured at 410.2 nm, was used as a measure of the yttrium concentration in the sample. A similar procedure was used for the analyses of 18 generated samples, 6 each at approximately 0.5, 1, and 2 times the OSHA standard level. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S200.

Modification

P&CAM 173 was modified by use of perchloric acid to aid in decomposition of the filter.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the nickel report (Reference No. 1). Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing solutions of yttrium in dilute hydrochloric acid and nitric acid at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of approximately 1.4 liters per minute for 360 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate yttrium was determined by collecting eight filter samples at an air sample concentration of 2.211 mg/cu m (2X OSHA standard level). The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was 1.00 when the test atmosphere was sampled for 360 minutes. Therefore, no correction for collection efficiency is necessary.

Collection Efficiency

2S Level

Front Filter Found, µg	Backup Filter Found, µg	Collection Efficiency
1110	N.D.	1.00
1140	N.D.	1.00
1090	N.D.	1.00
1110	N.D.	1.00
1070	N.D.	1.00
1135	N.D.	1.00
1080	N.D.	1.00
1070	N.D.	1.00

N.D. = Not Detected (< 10 µg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.019$ $\overline{CV}_2 = 0.019$ $\overline{CV}_T = 0.054$

Data Sheet: Yttrium S200

Analysis

Level	0.5S		1S			2S		
µg added	µg found	A.M.R.	µg added	µg found	A.M.R.	µg added	µg found	A.M.R.
270.0	267.5	0.991	540	530	0.981	1080	1070	0.991
270.0	267.5	0.991	540	515	0.954	1080	1075	0.995
270.0	255.0	0.944	540	513	0.950	1080	1100	1.018
270.0	260.0	0.963	540	505	0.935	1080	1075	0.995
270.0	255.0	0.944	540	520	0.963	1080	1075	0.995
270.0	257.5	0.954	540	503	0.931	1080	1053	0.975
n =		6			6			6
mean		0.965			0.952			0.995
std dev		0.022			0.018			0.014
CV_1		0.023			0.019			0.014

$\overline{CV}_1$ 0.019

$\overline{CV}_{A+\overline{AMR}}$ 0.021

The average Analytical Method Recovery (A.M.R.) at each level was used to calculate the corr. µg at each level in the Sampling and Analysis Table.

Data Sheet: Yttrium S200

Sampling and Analysis

Test Level	Found			
	µg	Corr µg	Liters	mg/cu m*
0.5S	265	275	508	0.541
	255	264	504	0.524
	255	264	504	0.524
	258	267	504	0.530
	255	264	502	0.526
	258	267	504	0.530
			n = 6	
			mean	0.529
			std dev	0.006
			CV_2	0.011
1S	528	555	508	1.092
	530	557	504	1.105
	518	544	504	1.079
	500	525	504	1.042
	510	536	502	1.068
	528	555	504	1.101
			n = 6	
			mean	1.081
			std dev	0.024
			CV_2	0.022
2S	1110	1116	508	2.197
	1140	1146	504	2.274
	1090	1096	504	2.175
	1110	1116	504	2.214
	1070	1075	502	2.141
	1135	1141	504	2.264
			n = 6	
			mean	2.211
			std dev	0.051
$\overline{CV}_2$ 0.019			CV_2	0.023

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, Nickel, No. S206, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: Tellurium, No. S204

OSHA Standard: 0.1 mg/cu m

Chemical Used for Validation: Tellurium
Johnson-Matthey

Procedure

The general procedure is described in NIOSH Method No. S204 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations representing 670-liter air samples at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in dilute nitric acid was added to 37-mm/0.8 micron Type AA Millipore filters. The filters containing the samples were digested with concentrated nitric and perchloric acids. The analyte was dissolved in dilute nitric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer. The absorbance, measured at 214.3 nm, was used as a measure of the tellurium concentration in the sample. A similar procedure was used for the analysis of 18 generated samples, six each at approximately 0.5, 1, and 2 times the OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S204.

Modification

P&CAM 173 was modified by use of perchloric acid to aid in decomposition of the filter.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the Nickel report (Reference No. 1). Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing solutions of tellurium in dilute nitric acid at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of approximately 1.4 liters per minute for 480 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate tellurium was determined by collecting eight filter samples at an air sample concentration of 0.24 mg/cu m (2X OSHA standard level). The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was considered to be 1.00 when the test atmosphere was sampled for 480 minutes. Therefore, no correction for collection efficiency is necessary.

Collection Efficiency

2X Level

Front Filter Found µg	Backup Filter Found µg	Collection Efficiency
159.0	N.D.	1.00
159.0	N.D.	1.00
161.0	N.D.	1.00
162.5	N.D.	1.00
162.0	N.D.	1.00
165.5	N.D.	1.00
164.0	N.D.	1.00
156.0	N.D.	1.00

N.D. = Not Detected (< 1.5 µg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for tellurium as in Reference No. 3.

The sampling and analysis data gave a chi squared value of 11.2 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. Therefore, CV_T is calculated only on the data at the 1X level.

$$CV_T = \sqrt{CV_2^2 + (0.05)^2} = 0.055$$

where:

CV_2 = Coefficient of Variation at the 1X level for Sampling & Analysis = 0.023

0.05 = pump error

Data Sheet: Tellurium S204

Analysis

Level	0.5S			1S			2S	
µg added	µg found	A.M.R.	µg added	µg found	A.M.R.	µg added	µg found	A.M.R.
36.0	35.0	0.972	72.0	69.5	0.965	144.0	145.0	1.007
36.0	37.0	1.028	72.0	74.0	1.028	144.0	141.0	0.979
36.0	33.5	0.931	72.0	74.0	1.028	144.0	145.0	1.007
36.0	37.5	1.042	72.0	74.0	1.028	144.0	141.0	0.979
36.0	36.0	1.000	72.0	71.5	0.993	144.0	139.5	0.969
36.0	33.0	0.917	72.0	73.5	1.021	144.0	144.0	1.000
n =		6			6			6
mean		0.982			1.010			0.990
std dev		0.051			0.026			0.016
CV_1		0.052			0.026			0.016

$\overline{CV}_1$ 0.035

$\overline{CV}_{A+\overline{AMR}}$ 0.038

Based on the above results, no analytical method recovery (A.M.R.) correction is necessary.

Data Sheet: Tellurium S204

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.0340	674	0.0504
	0.0300	672	0.0446
	0.0340	672	0.0506
	0.0370	672	0.0551
	0.0335	670	0.0500
	0.0310	672	0.0461
		n = 6	
		mean	0.0495
		std dev	0.0037
		CV_2	0.075
1S	0.0555	674	0.0823
	0.0555	672	0.0826
	0.0580	672	0.0863
	0.0580	672	0.0863
	0.0570	670	0.0851
	0.0555	672	0.0826
		n = 6	
		mean	0.0842
		std dev	0.0019
		CV_2	0.023
2S	0.1590	674	0.236
	0.1590	672	0.237
	0.1610	672	0.240
	0.1625	672	0.242
	0.1620	670	0.242
	0.1655	672	0.246
		n = 6	
		mean	0.240
		std dev	0.004
$\overline{CV}_2$ 0.046		CV_2	0.017

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Nickel, No. S206, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Calcium Oxide, No. S205
OSHA Standard:	5 mg/cu m
Chemical Used for Validation:	Calcium oxide (Bakers Analyzed Reagent) Solutions used for validation were standardized by EDTA titration.

Procedure

The general procedure is described in NIOSH Method No. S205 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations similar to those representing 85-liter samples at 0.5, 1.0, and 2.0 times the OSHA standard. The appropriate aliquot of a solution of the analyte in dilute HCl was added to 37-mm/0.8-micron Type AA Millipore filters. The filters were digested with concentrated nitric and perchloric acids, and the residue was dissolved in hydrochloric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer. The absorbance, measured at 422.7 nm, was used to measure the calcium oxide concentration in the sample. A similar procedure was used for the analyses of 18 generated samples, 6 each at approximately 0.5, 1 and 2 times the OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S205.

Modification

P&CAM 173 was modified by use of perchloric acid to aid in decomposition of the filter.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the Nickel report (Reference No. 1). Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing solutions of calcium oxide in dilute HCl at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of approximately 1.4 liters per minute for 60 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered to be equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate calcium oxide was determined by collecting eight filter samples at an air sample concentration of 4.9 mg/cu m. The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was 1.00 when the test atmosphere was sampled

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for 60 minutes. The data on the backup filter was obtained on a final assay solution volume of 5 ml rather than 100 ml as recommended in the NIOSH Method S205.

No correction for collection efficiency is necessary.

Collection Efficiency of Calcium Oxide

Front Filter Found μg	Backup Filter Found μg	Collection Efficiency
374	N.D.	1.00
395	N.D.	1.00
409	2	1.00
416	N.D.	1.00
416	N.D.	1.00
416	3	0.99
437	2	1.00
411	2	1.00

N.D. = Not detected (< 2 μg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for calcium oxide as in Reference No. 3.

The sampling and analysis data gave a chi squared value of 10.3 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. Therefore, CV_T is calculated only on the data at the 1X level.

$$CV_T = \sqrt{CV_2^2 + (0.05)^2} = 0.063$$

where:

CV_2 = Coefficient of Variation at the 1X level for Sampling and Analysis = 0.039

(0.05) = pump error

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Data Sheet: Calcium Oxide S205

Analysis

Level	0.5S		1S			2S		
mg added	mg found	A.M.R.	mg added	mg found	A.M.R.	mg added	mg found	A.M.R.
0.218	0.223	1.023	0.460	0.462	1.004	0.892	0.902	1.011
0.218	0.223	1.023	0.460	0.448	0.974	0.892	0.909	1.019
0.218	0.217	0.995	0.460	0.455	0.989	0.892	0.867	0.972
0.218	0.217	0.995	0.460	0.448	0.974	0.892	0.902	1.011
0.218	0.223	1.023	0.460	0.462	1.004	0.892	0.874	0.980
0.218	0.210	0.963	0.460	0.455	0.989	0.892	0.881	0.988
n =		6			6			6
mean		1.004			0.989			0.997
std dev		0.024			0.013			0.019
CV_1		0.024			0.013			0.019

$\overline{CV}_1$ 0.019

$\overline{CV}_{A+\overline{AMR}}$ 0.021

Based on the above results, no analytical method recovery (A.M.R.) correction is necessary.

Data Sheet: Calcium Oxide S205

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m
0.5S	0.2099	82.7	2.538
	0.2029	82.1	2.471
	0.2204	83.1	2.652
	0.2204	84.0	2.624
	0.2204	82.1	2.685
	0.2170	83.5	2.599
		n = 6	
		mean	2.595
		std dev	0.079
		CV_2	0.030
1S	0.374	82.7	4.52
	0.395	82.1	4.81
	0.409	83.1	4.92
	0.416	84.0	4.95
	0.416	82.1	5.07
	0.416	83.5	4.98
		n = 6	
		mean	4.88
		std dev	0.19
		CV_2	0.039
2S	0.843	82.7	10.19
	0.829	82.1	10.10
	0.850	83.1	10.23
	0.850	84.0	10.12
	0.898*	82.1*	10.94*
	0.850	83.5	10.18
		n = 5	
		mean	10.16
		std dev	0.05
		CV_2	0.005

* These values were excluded from statistical analysis because they did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

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References

1. Backup Data Report, Nickel, No. S206, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Nickel, Metal and Soluble Compounds (as Ni), No. S206
OSHA Standard:	1 mg/cu m
Chemical Used for Validation:	Nickel Nitrate Hexahydrate (Bakers Analyzed Reagent) Solutions used for validation were standardized by precipitation and weighing nickel as the dimethylglyoxime.

Procedure

The general procedure is described in NIOSH Method No. S206 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations similar to those representing a 90-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of an aqueous solution of nickel nitrate was added to 37-mm/0.8-micron Type AA Millipore filters. The filters containing the samples were digested with concentrated nitric and perchloric acids. The analyte was dissolved in nitric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer. The absorbance, measured at 232.0 nm, was used as a measure of the nickel concentration in the sample. A similar procedure was used for the analysis of 18 generated samples, 6 each at approximately 0.5, 1, and 2 times the OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S206.

Modification

P&CAM 173 was modified by use of perchloric acid to aid in decomposition of the filter.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to this report. Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing aqueous solutions of nickel nitrate at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of approximately 1.4 liters per minute for 60 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate nickel was determined by collecting eight filter samples at an air sample concentration of 2.2 mg/cu m (2X OSHA standard

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level). The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was considered to be 1.00 when the test atmosphere was sampled for 60 minutes. Therefore, no correction for collection efficiency is needed. The data on the backup filter was obtained on a final assay solution volume of 5 ml rather than 25 ml as recommended in the NIOSH Method S206.

COLLECTION EFFICIENCY OF NICKEL

μg		
Front	Backup	Collection Efficiency
190	N.D.	1.00
193	N.D.	1.00
187	N.D.	1.00
185	N.D.	1.00
180	N.D.	1.00
195	N.D.	1.00
190	N.D.	1.00
185	N.D.	1.00

N.D. = Not Detected (< 1.5 μg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 1.

$\overline{CV}_1 = 0.024$ $\overline{CV}_2 = 0.026$ $\overline{CV}_T = 0.057$

Data Sheet: Nickel, Metal and Soluble Compounds, S206

Analysis

Level	0.5S		1S			2S		
µg added	µg found	A.M.R.	µg added	µg found	A.M.R.	µg added	µg found	A.M.R.
44.5	45.7	1.027	89.0	88.8	0.998	178.0	173.8	0.976
44.5	45.0	1.011	89.0	86.8	0.975	178.0	162.5	0.913
44.5	44.5	1.000	89.0	88.0	0.989	178.0	173.3	0.974
44.5	45.0	1.011	89.0	85.8	0.964	178.0	163.8	0.920
44.5	44.3	0.996	89.0	89.5	1.006	178.0	165.8	0.931
44.5	44.5	1.000	89.0	85.8	0.964	178.0	176.3	0.990
n =		6			6			6
mean		1.007			0.983			0.951
std dev		0.011			0.018			0.033
CV_1		0.011			0.018			0.035

$\overline{CV}_1$ 0.024

$\overline{CV}_{A+\overline{AMR}}$ 0.026

Based on the above results, no Analytical Method Recovery is necessary.

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Data Sheet: Nickel, Metal and Soluble Compounds S206

Sampling and Analysis

Test Level	---------- Found ----------		
	mg	Liters	mg/cu m*
0.5S	0.0370	85.4	0.433
	0.0385	85.0	0.453
	0.0385	85.0	0.453
	0.0370	85.5	0.433
	0.0385	84.7	0.455
	0.0385	85.0	0.453
		n = 6	
		mean	0.447
		std dev	0.011
		CV_2	0.025
1S	0.0820	85.4	0.960
	0.0820	83.3	0.984
	0.0800	85.0	0.941
	0.0850	85.0	1.000
	0.0843	85.5	0.986
	0.0843	84.7	0.995
		n = 6	
		mean	0.978
		std dev	0.023
		CV_2	0.024
2S	0.183	85.4	2.143
	0.170	83.3	2.041
	0.183	85.0	2.153
	0.175	85.0	2.059
	0.175	85.5	2.047
	0.170	84.7	2.007
		n = 6	
		mean	2.075
		std dev	0.059
$\overline{CV}_2$ 0.026		CV_2	0.028

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Attachment to Nickel S206 Backup Data Report

Inorganic Particulate Generation System

A line drawing of the atmosphere generation system is shown in Figure 1. It has a 25-mm O.D. glass vertical transport tube. A short distance downstream of the entrance of this transport tube is a gas dispersion tube which is placed directly in the middle of the tube. This gas dispersion tube serves to dilute the aerosol and to provide uniform mixing with minimal wall loss. The annular clearance is such that the Reynold's number of approximately 2500 is obtained with a total design flow of 24 liters per minute. Normally the test aerosol is diluted by a factor of two in this mixing system. Gas flows to all parts of the system are controlled by means of critical flow orifices.

Approximately 6 inches downstream of the mixing section, the sample is split into two fractions by means of a sampling tube placed in the middle of the main transport tube. The main body of the aerosol is passed through a 12-liter per minute critical flow orifice to maintain the design flow of 24 liters per minute in the system. The 12-liter per minute orifice is protected by a 47-mm 0.8-μ pore size filter. It was expected that this filter would also provide basis for an "independent" determination of aerosol mass in the air stream. However, this concept was unsatisfactory and was abandoned largely because the ratio of masses of aerosol found in the two fractions was not constant.

The fraction which is removed is transported to a spherical sampling section with eight sampling ports which are arranged so that there is a minimum sampling bias between each port. The test samples are collected on 37-mm diameter filters contained in the standard plastic filter holders. The sampling rate is controlled by precision drilled saphire critical flow orifices with a flow rate of 1.4 liters per minute. The orifices are protected by absolute filters downstream of the test filters. Before each test, the sampling system is checked for leaks by pulling a high vacuum on the system and measuring the leak rate with a vacuum gauge.

The individual filter collectors (8) were determined to have flow rates as follows:

Position	Size	Flow rate (liter/min)
1	37 mm	1.423
2	"	1.389
3	"	1.417
4	"	1.416
5	"	1.425
6	"	1.411
7	"	1.416
8	"	1.424
Subtotal		11.321
9	47	11.73

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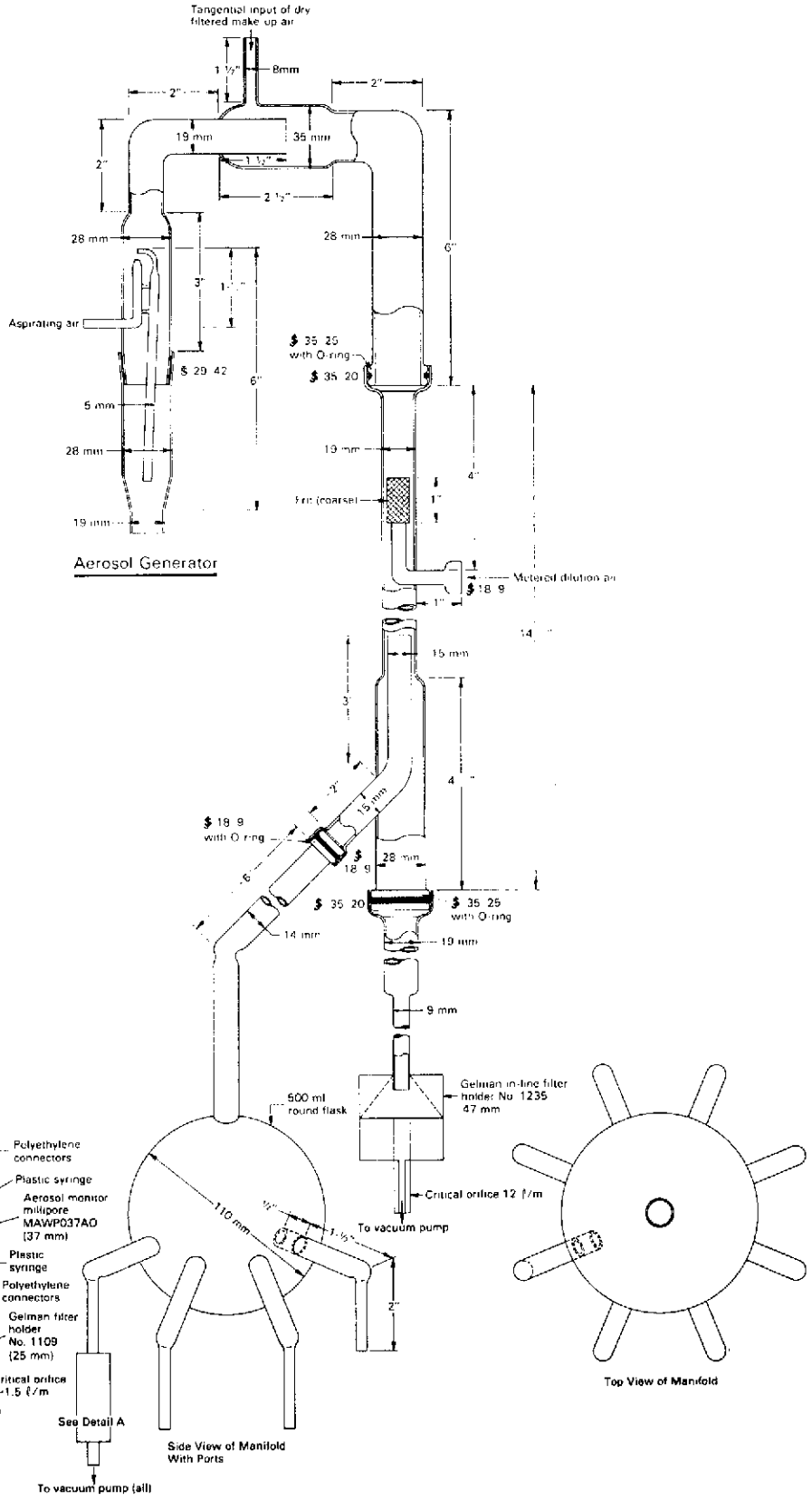
FIGURE 1. AEROSOL GENERATION SYSTEM



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The bulk of the inorganic aerosols are produced by the nebulization of soluble salt using the nebulizer shown in Figure 1. The nebulizer is designed to have a flow rate of approximately 5 liters per minute at an atomizing pressure of 5 psi. The flow is monitored by a precision test gauge and the atomizing air is saturated to prevent concentration change of the test solution during the run. The nebulizer produces a test aerosol at a rate of 35 milligrams per minute with a mass median diameter of approximately 3 micrometers. Immediately downstream of the nebulizer is a cyclone-type aerosol drier to evaporate volatile constituents from the particles. Dry filtered air is added to this section at the periphery to minimize wall loss and to reduce the particle size of the test aerosol by evaporation of the solvent. The relationship between the aerosol particle sizes of a nebulized solution containing 1% solids and the dried residue after evaporation of the solvent is given by

$$d_1 \neq d_2$$

$$D_2 = .215\, D_1 \left(\frac{d_1}{d_2} \right)$$

where: D_1 = Diameter of the 1% solid in solution

D_2 = Diameter of the dried solid

d_1 = Density of 1% solid in solution

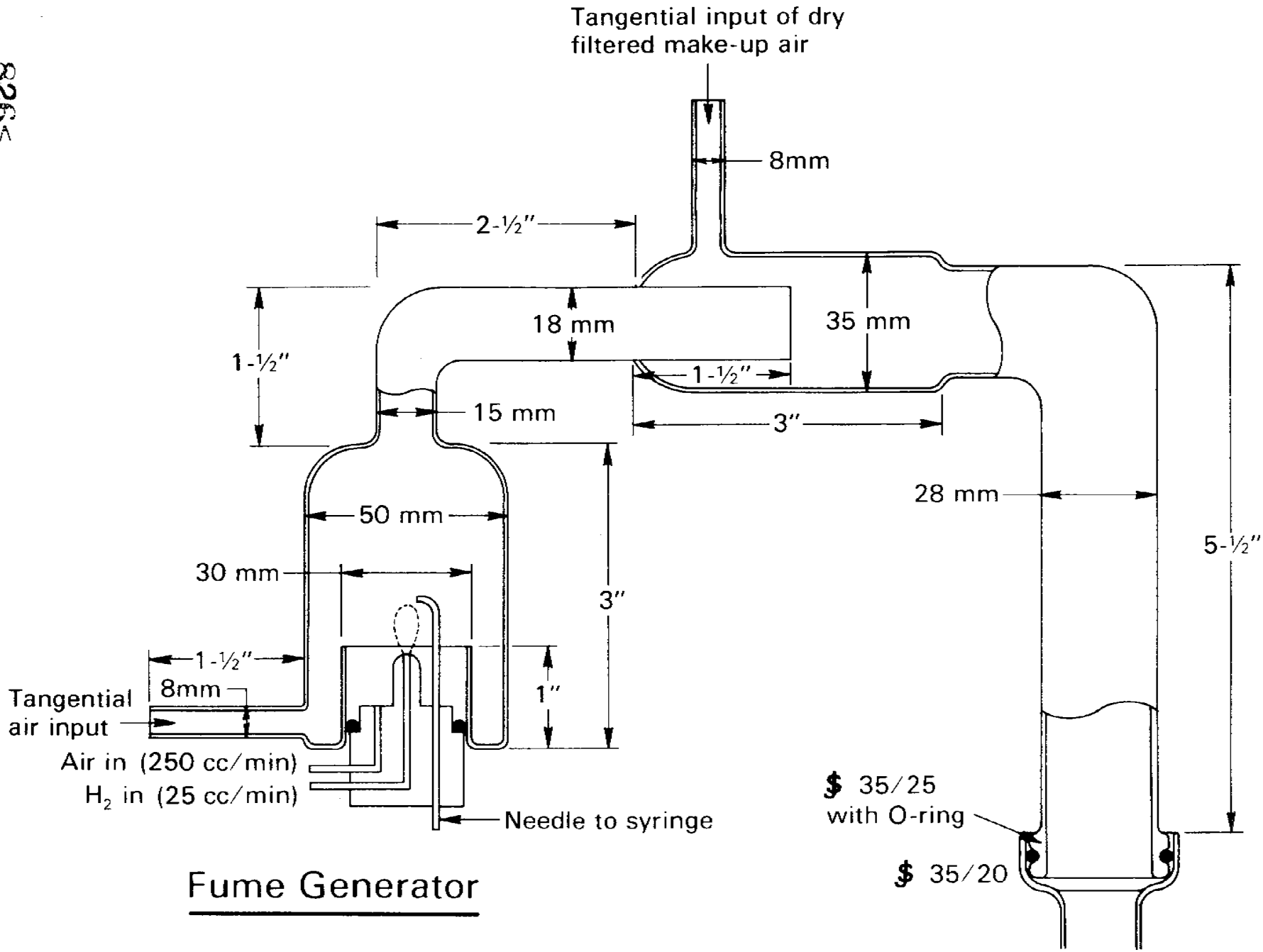
d_2 = Density of dried solid

It is estimated that the test aerosol would have a mass median diameter (MMD) between 0.5 to 1.0 micrometer. Particles in this size range behave quite similar to a gas and are not subject to gravitational losses. Inertial losses are minimal for the velocities encountered in the transport system.

The generator for metallic fumes, such as Fe, Cd, Cu, and Co, consists of a hydrogen burner from a gas chromatograph detector and is shown in Figure 2. A glass mantle and dilution section attaches to the burner. The test materials may be organometallics dissolved in white gasoline and fed into the flame by means of a long hypodermic needle attached to a Sage instrument Model 352 syringe pump and a gas-tight syringe. It would have been desirable to introduce the fuel containing the metallic constituent along with the hydrogen flame; however, the pressure was too great for the syringe pump. The fuel mixture is introduced into a cool portion of the flame to reduce evaporation which would concentrate the metallic constituent in the hypodermic delivery tube.

A Wright Dust Feeder is available to disperse powders. Samples to be dispersed in the apparatus are compressed into a special holder. In operation, the holder and the dust compact are slowly rotated and driven against a stationary scraper blade which continuously removes dust from the compact surface at a uniform rate. The rate of dust delivered from the feeder may be varied by changing gears in the compact advance mechanism. The powder is entrained in an air stream and as it leaves the feeder it passes through a jet which impinges any large agglomerates on to an impaction plate which tends to dispense them into individual particles.

FIGURE 2. FUME GENERATOR



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S206-9

Backup Data Report

Substance: Tributyl Phosphate, No. S208

OSHA Standard: 5.0 mg/cu m

Chemical Used for Validation: Tributyl Phosphate, Aldrich Chemical Co., Reagent Grade

Procedure

The general procedure used is described in NIOSH Method No. S208 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 100-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in ether was added to 37-mm Type AA Millipore filters. The analyte was extracted from the filter with ether and analyzed in a Varian 2700 Gas Chromatograph with a flame photometric detector and an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System I Computing Integrator was used for area measurements and determination of sample concentration. A set of 18 generated samples, 6 at each of the 0.5, 1 and 2X the OSHA standard concentration, was collected and analyzed similarly. Details of the analytical procedure may be found in Section 8 of the NIOSH Method No. S208 and in the Butyl Acetate S47 Backup Data Report and Attachment.

Modification

P&CAM 127 was modified to suit the needs of this particular analysis. A flame photometric detector with a phosphorus-filter (526 nm) was used for specificity and sensitivity and ether was substituted for carbon disulfide in order to minimize solvent interference; carbon disulfide gives a strong response with the flame photometric detector.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by direct atomization of tributyl phosphate. The system used for the generation of test atmospheres of tributyl phosphate is the same unit as that used for the triphenyl phosphate and is described in the S210 Triphenyl Phosphate Backup Data Report; the basic components of this generator are reproduced again in Figures 1 and 2. Approximately 200-300 ml of tributyl phosphate was added to the 500-ml, three-neck round-bottom flask. The liquid was nebulized by passing a regulated amount of air through the Laskin nozzle (Figure 1); the air flow through the nozzle and the dilution air flow through the dilution tube were adjusted and balanced until the desired mainline concentration was produced. The other components of the generation/dilution system are described in detail in the S97

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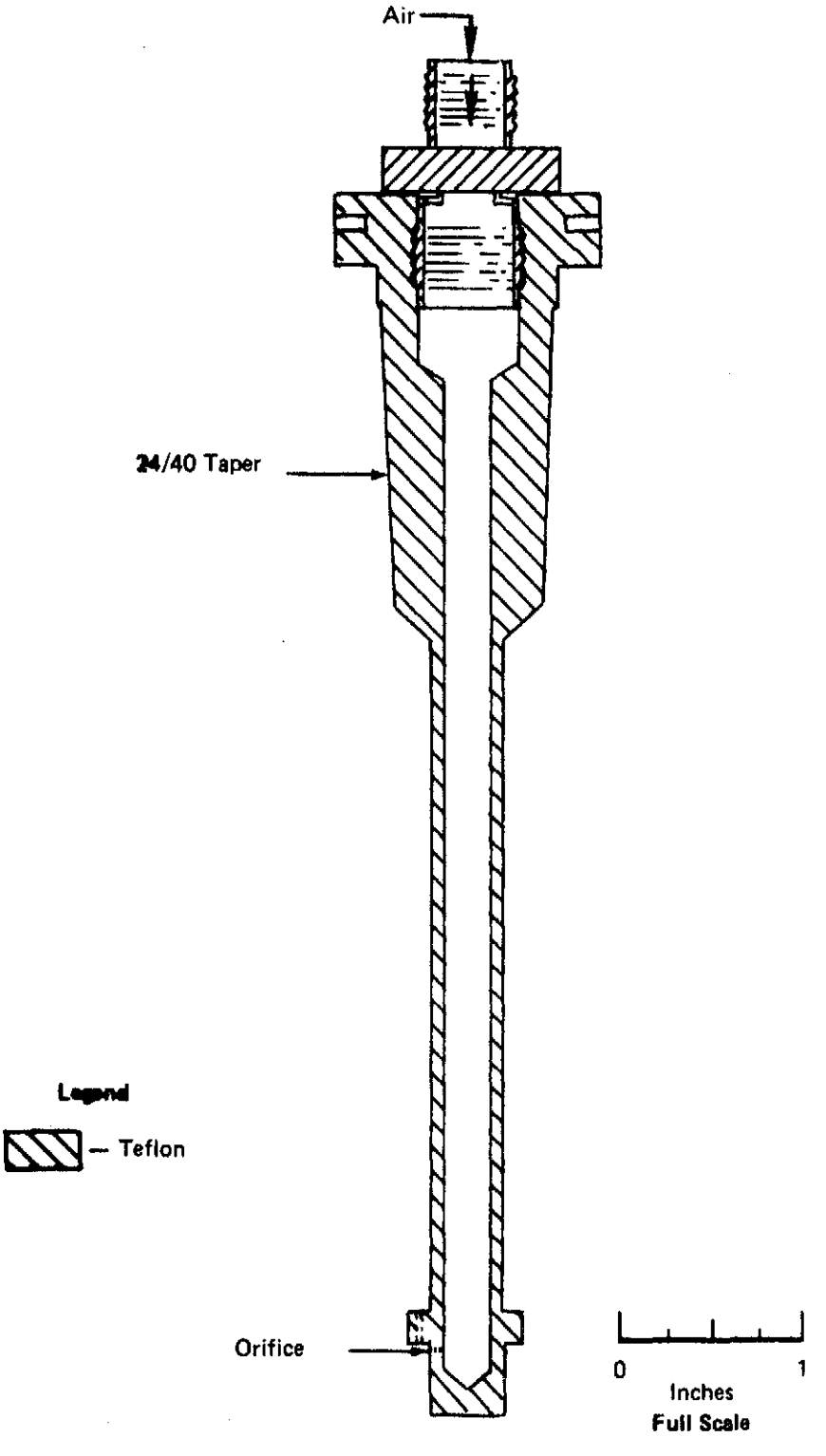

FIGURE 1 CROSS SECTIONAL VIEW OF LASKIN TYPE NOZZLE

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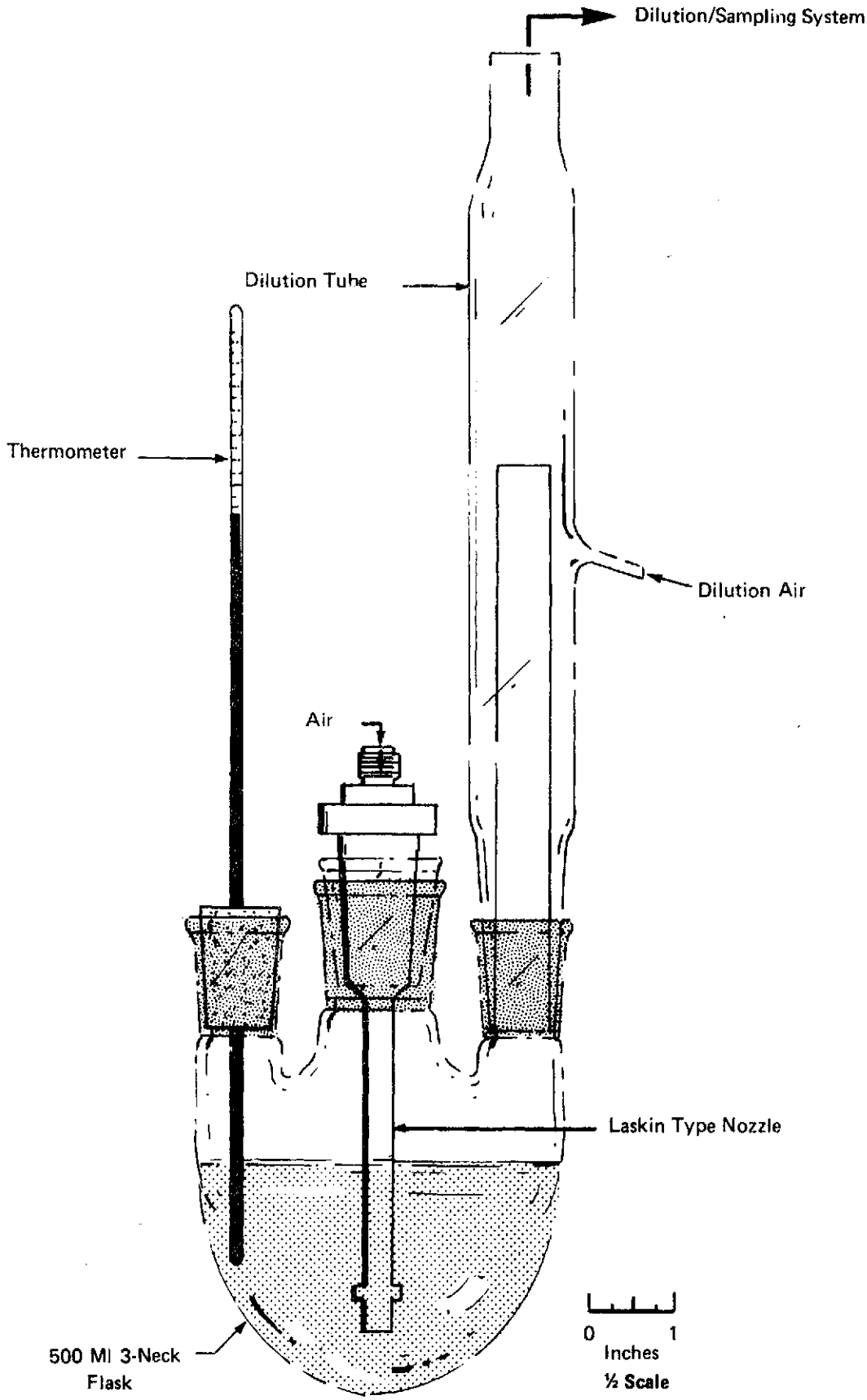

FIGURE 2 CROSS-SECTIONAL VIEW OF NEBULIZER/DILUTION SYSTEM

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Octachloronaphthalene Backup Data Report and Attachment. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5X the OSHA standard level. A set of 18 samples, 6 at each of the three test levels, was collected simultaneously at 1.5 liters per minute for 66 minutes (100 liters).

Collection Efficiency

To determine the collection efficiency of the 37-mm Type AA Millipore filter for tributyl phosphate aerosols, two filters were mounted in the three-piece filter cassette such that the front and backup filters were physically separated and only the backup filter was supported by the cellulose backup pad. Six such sample filter cassettes were used to determine the collection efficiency for an air sample concentration of 12.6 mg/cu m at a sampling rate of 1.5 liters per minute for 66 minutes. The front filter, the backup filter, and the backup pad were analyzed separately and the relative amount of tributyl phosphate collected in the front and backup filters and the pad were determined, based on the total quantity found. The data summarized in Table 1 show that the average collection efficiency for tributyl phosphate was 100% for the conditions described above. The collection efficiency was also found to be 99.6% when a test atmosphere containing 9.3 mg/cu m was sampled at 1.5 liters per minute for 66 minutes; the atmospheric temperature range and pressure for these experiments were 19-20°C and 761 mm Hg.

There are indications that the collection efficiency of tributyl phosphate may be dependent on atmospheric temperature and pressure conditions because of some tendency to vaporize. This observation is based on the data from analytical studies conducted, whereby 973 µg of tributyl phosphate was added to Type AA Millipore filters and these filters were then mounted in filter cassettes preparatory to passing controlled amounts of air through the filters. The data for two experimental studies conducted on different days are shown in Table 2. The amounts of tributyl phosphate left on the filters after passing 180 and 100 liters of air through the filters were 97% and 96% respectively; in the latter case, the remaining 4% was found on the backup pad.

Although the relative differences in measured "collection efficiencies" for 100-liter samples are not large -- 100% at 19°C, 99.6% at 20°C, 95.8% at 23°C -- these observations are noted because the degree of distribution between tributyl phosphate particulate and vapor may be significantly different at higher temperatures. It is expected that at 2X OSHA standard and for a 100-liter sample, the backup pad can absorb the tributyl phosphate vapor without significant loss when the vapor is present in amounts of 10% or less relative to the total (particulate plus vapor) tributyl phosphate present.

Table 1

Collection Efficiency of Tributyl Phosphate
on 37-mm Type AA Millipore Filters

A. Test Concentration: 12.6 mg/cu m
Sample Volume: 100 liters at 1.5 liters per minute
Atmospheric Conditions: 19°C and 761 mm Hg

µg Found				
Front	Backup Filter	Backup Pad	Total	% Collected in Front
1185	2	ND	1187	99.8
1216	ND	ND	1216	100.0
1349	ND	ND	1349	100.0
1222	ND	ND	1222	100.0
1225	ND	ND	1225	100.0
1451	ND	ND	1451	100.0

Average Collection Efficiency . . . 100.0%

B. Test Concentration: 9.3 mg/cu m
Sample Volume: 100 liters at 1.5 liters per minute
Atmospheric Conditions: 20°C and 761 mm Hg

µg Found				
Front	Backup Filter	Backup Pad	Total	% Collected in Front
896	6	6	908	98.7
947	7	6	960	98.6
943	ND	ND	943	100.0
938	ND	ND	938	100.0
928	ND	ND	928	100.0
905	ND	ND	905	100.0

Average Collection Efficiency . . . 99.6

ND - Not detectable; the lower limit of detection is 2 µg in a total volume of 10 ml.

Table 2

Analytical Studies on Volatility of Tributyl Phosphate

Experiment A

Amount Added: 973 µg
Atmospheric Conditions: not available

Spiked Filters (Controls)		Spiked Filters + 180 Liters Air	
µg Found	% Found*	µg Found	% Found*
968	99.5	955	98.2
953	97.9	930	95.6
970	99,6	954	98.0
972	99.9	949	97.5
Average . .	99.2%	Average . .	97.3%

Experiment B

Amount Added: 973 µg
100 Liters of air was passed through filters.
Atmospheric Conditions: 23°C and 754 mm Hg

----- µg Found -------			% Residual*
Filter	Pad	Total	on Filter
934	42	976	96.0
948	37	985	97.4
935	37	972	96.1
919	44	963	94.5
926	44	970	95.2
928	43	971	95.4
		Average	95.8%

* All calculations were based on 973 µg added.

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Discussion

Other collection media, such as Lot 105 and Lot 104 charcoal and ethyl acetate in impingers were tested for collecting tributyl phosphate vapor; none of these was suitable. The DE from both lots of charcoal were low, averaging about 25% for 230 µg of tributyl phosphate added when solvents such as ether, methanol and isopropyl alcohol were used for desorption. Ethyl acetate/impingers do not collect tributyl phosphate efficiently.

In order to address the probable presence of tributyl phosphate vapor, a double filter cassette arrangmeent is recommended when sampling, particularly at atmospheric temperatures greater than 23°C. This means using a front filter/pad and backup filter/pad mounted in separate cassette filter holders and connected in series using a short piece of tubing. The front filter and pad are then analyzed together and the backup filter and pad are analyzed similarly.

All of the validation data on the analysis and the sampling and analysis precision are based on data derived from the analysis of filters only, i.e., without the supporting cellulose pads. Some studies were conducted to test the comparative recovery and precision obtained when sample-containing filters were extracted with or without the backup pad. Twelve filters were spiked with 486 µg of tributyl phosphate. Six filters were used as controls, while each of the other six filters was combined with a cellulose pad and then extracted with ether. The data shown in Table 3 indicate that the precision and recovery obtained in either case are comparable. A separate study with cellulose pads spiked with 97 µg of tributyl phosphate and extracted with ether also gave an average recovery of 96% with equally good precision based on the analysis of six samples.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for tributyl phosphate as described in Reference 2.

The sampling and analysis data gave a chi squared value of 12.32 indicating that the hypothesis of equal variance may be rejected at P (probability) less than 0.01. The data for tributyl phosphate show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures are described in Reference 1; the data are shown in Tables 4 and 5.

$$\overline{CV}_1 = 0.0146 \qquad \overline{CV}_2 = 0.0572 \qquad \overline{CV}_T = 0.0762$$

Since the collection efficiency was found to be 100% and no bias was found in the analytical recovery studies, average recovery = 100%, $\overline{CV}_T$ is a satisfactory measure of precision and accuracy.

Table 3

Comparison of Recovery and Precision for Filters
Extracted in the Presence or Absence of Backup Pads

------ Filter Only -------			----- Filter & Pad -------		
µg added	µg found	Recovery	µg added	µg found	Recovery
486	466	0.959	486	467	0.961
486	484	0.996	486	463	0.953
486	503	1.035	486	473	0.973
486	476	0.979	486	488	1.004
486	480	0.988	486	444	0.914
486	481	0.990	486	Sample Lost	-
n =		6			5
mean		0.991			0.961
std dev		0.0250			0.0327
CV_1		0.0253			0.0340

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Table 4

Data Sheet: Tributyl Phosphate, S208
(37-mm Type AA Millipore Filter)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
233.5	227.8	0.976	486	477	0.981	973	954	0.980
233.5	238.4	1.021	486	489	1.006	973	973	1.000
233.5	235.8	1.010	486	487	1.002	973	973	1.000
233.5	234.1	1.003	486	488	1.004	973	984	1.011
233.5	237.6	1.018	486	488	1.004	973	969	0.996
233.5	239.7	1.027	486	499	1.027	973	975	1.002
n =		6			6			6
mean		1.009			1.004			0.998
std dev		0.0183			0.0146			0.0102
CV_1		0.0181			0.0145			0.0102

$\overline{CV}_1$ 0.0146

$\overline{CV}_{A+\overline{DE}}$ 0.0158

Table 5

Data Sheet: Tributyl Phosphate, S208
(37-mm Type AA Millipore Filter)

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	277.2	100.8	2.750
	272.7	100.5	2.713
	272.0	100.1	2.717
	272.3	100.7	2.704
	278.2	100.4	2.771
	272.7	101.2	2.695
		n = 6	
		mean	**2.725**
		std dev	0.0293
		CV_2	0.0107
1S	634	101.0	6.28
	704	101.1	6.96
	671	100.6	6.67
	734	101.4	7.24
	647	101.8	6.36
	636	101.2	6.28
		n = 6	
		mean	6.63
		std dev	0.400
		CV_2	0.0603
2S	1185	101.0	11.73
	1216	100.8	12.06
	1349	100.9	13.37
	1222	100.8	12.12
	1225	100.6	12.18
	1451	101.7	14.27
		n = 6	
		mean	12.62
		std dev	0.983
		CV_2	0.0779
		$\overline{CV_2}$	0.0572

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References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract No. CDC-99-74-45.

Backup Data Report

Substance: Triorthocresyl Phosphate, No. S209

OSHA Standard: 0.1 mg/cu m

Chemical Used for Validation: Triorthocresyl Phosphate, K & K Chemicals, 95%

Procedure

The general procedure used is described in NIOSH Method No. S209 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 100-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in ether was added to 37-mm Type AA Millipore filters. The analyte was extracted from the filter with ether and analyzed in a Varian 2700 Gas Chromatograph with a flame photometric detector and an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System I Computing Integrator was used for area measurements and determination of sample concentration. A set of 18 generated samples, 6 at each of the 0.5, 1 and 2X the OSHA standard concentration, was collected and analyzed similarly. Details of the analytical procedure may be found in Section 8 of the NIOSH Method No. S209 and in the Butyl Acetate S47 Backup Data Report and Attachment.

Modification

P&CAM 127 was modified to suit the needs of this particular analysis. A flame photometric detector with a phosphorus-filter was used for specificity and sensitivity and ether was substituted for carbon disulfide in order to minimize solvent interference; carbon disulfide gives a strong response with the flame photometric detector.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by direct atomization of liquid triorthocresyl phosphate. The system used for the generation of test atmospheres of triorthocresyl phosphate was the same unit as that used for the triphenyl phosphate and is described in the S210 Triphenyl Phosphate Backup Data Report; the basic components of this generator are reproduced again in Figures 1 and 2. Approximately 200-300 ml of triorthocresyl phosphate was added to the 500-ml three-neck round-bottom flask. The liquid was nebulized by passing a regulated amount of air through the Laskin nozzle (Figure 1); the air-flow through the nozzle and the dilution air flow through the dilution tube were adjusted and balanced until the desired mainline concentration was produced. The other components of the generation/dilution system

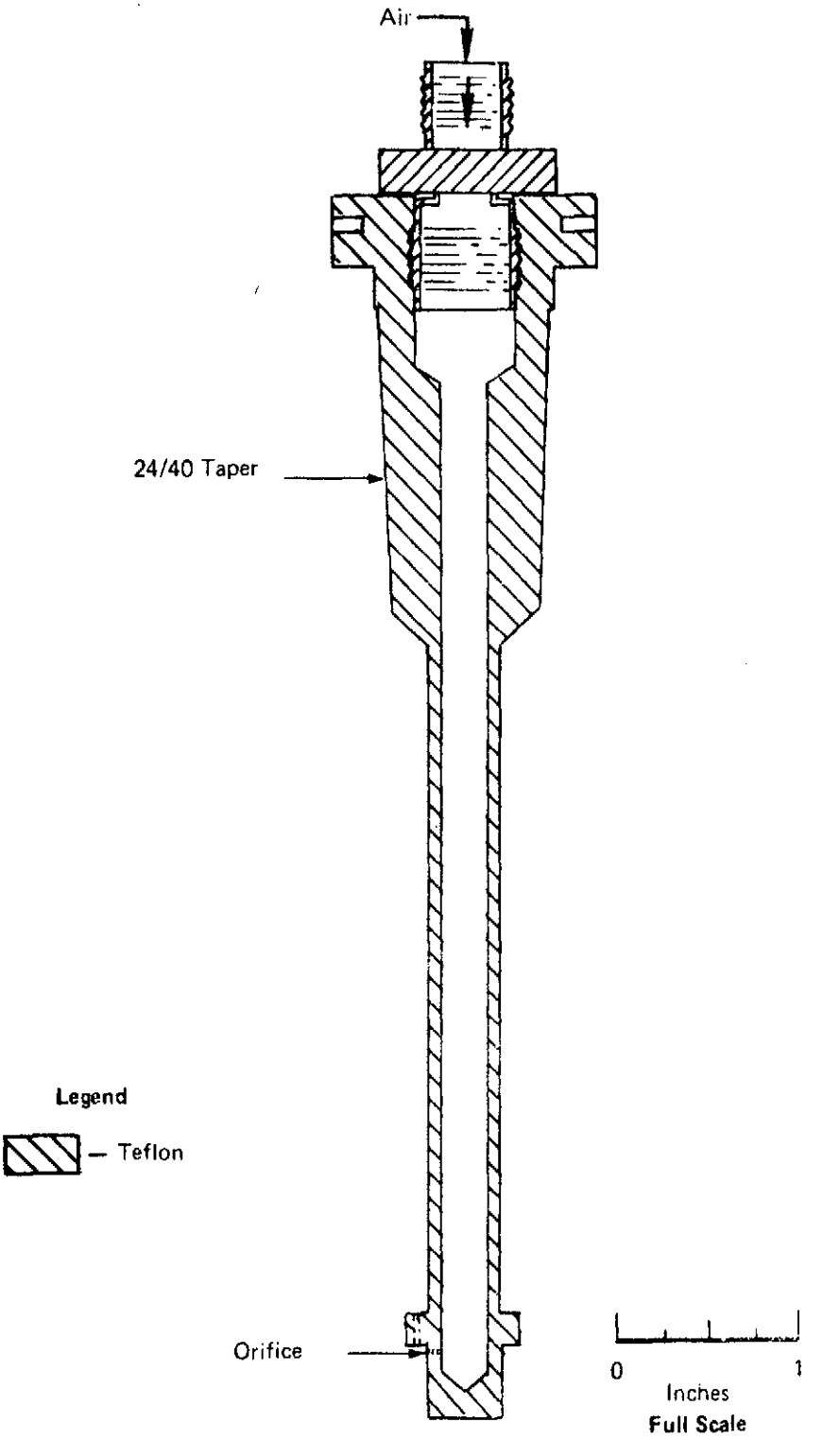

FIGURE 1 CROSS SECTIONAL VIEW OF LASKIN TYPE NOZZLE

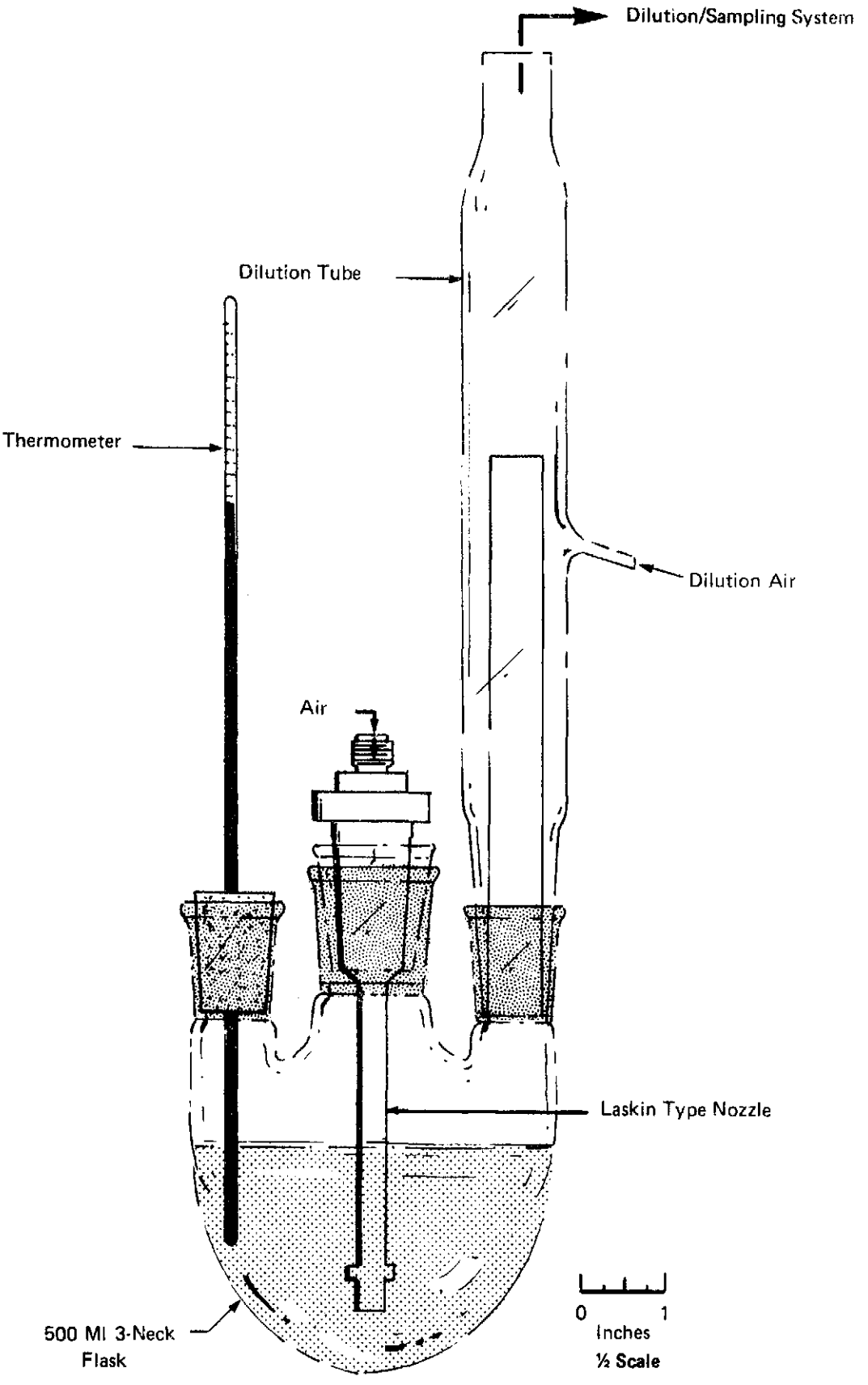

FIGURE 2 CROSS-SECTIONAL VIEW OF NEBULIZER/DILUTION SYSTEM

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are described in detail in the S97 Octachloronaphthalene Backup Data Report and Attachment. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5X the OSHA standard level. A set of 18 samples, 6 at each of the 3 test levels, was collected simultaneously at 1.5 liters per minute for 66 minutes (100 liters).

Collection Efficiency

To determine the collection efficiency of the 37-mm Type AA Millipore filter for triorthocresyl phosphate aerosols, two filters were mounted in the three-piece filter cassette such that the front and backup filters were physically separated and only the backup filter was supported by the cellulose backup pad. Six such sample filter cassettes were used to determine the collection efficiency for an air sample concentration of 0.17 mg/cu m at a sampling rate of 1.5 liters per minute for 66 minutes. Each filter was analyzed separately and the relative amount of triorthocresyl phosphate collected in the primary and backup filters was determined, based on the total quantity found in both filters. The data summarized in Table 1 show that the average collection efficiency for triorthocresyl phosphate was 98.8% including the data for another set of six samples equivalent to 150 liters for a test atmosphere concentration of 0.19 mg/cu m. Note also that when a test atmosphere containing 3.8 mg/cu m was sampled for 66 minutes at 1.5 liters per minute, the collection efficiency was found to be 99.5% based on the analysis of duplicate samples.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0234$ $\overline{CV}_2 = 0.0420$ $\overline{CV}_T = 0.0660$

Since the collection efficiency was found to be at least 98.8% and no bias was found in the analytical recovery studies, average recovery = 101%, $\overline{CV}_T$ is a satisfactory measure of both precision and accuracy.

Reference

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Table 1

Collection Efficiency* of Triorthocresyl Phosphate
on 37-mm Type AA Millipore Filters

A. Test Concentration: 0.17 mg/cu m
Sample Volume: 100 liters at 1.5 liters per minute

µg Found			
Front	Backup Filter & Pad	Total	% Collected in Front
16.17	0.084	16.254	99.5
14.82	0.333	15.153	97.8
17.47	0.419	17.889	97.7
18.25	0.064	18.314	99.7
18.09	0.148	18.238	99.2
17.22	0.163	17.383	99.1

Average Collection Efficiency 98.8%

B. Test Concentration: 0.19 mg/cu m
Sample Volume: 150 liters at 1.5 liters per minute

µg Found				
Front Filter	Backup Filter	Backup Pad	Total	% Collected on Front Filter
27.53	0.654	ND	28.184	97.7
26.31	0.204	ND	26.514	99.2
27.95	0.091	ND	28.041	99.7
29.23	0.239	1.140	30.609	95.5
26.71	ND	ND	26.710	100.0
27.32	ND	ND	27.320	100.0

Average Collection Efficiency 98.7%

*In a separate experiment and at a test atmosphere concentration of 3.8 mg/cu m for a 100-liter sample size, the collection efficiency was found to be 99.5% based on the analysis of duplicate samples.

ND - not detectable, the lower limit of detection is 0.05 µg in a total volume of 10 ml.

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Table 2

Data Sheet: Triorthocresyl Phosphate, S209

Analysis

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
5.85	6.14	1.050	11.70	11.63	0.994	23.40	23.65	1.011
5.85	6.18	1.056	11.70	11.79	1.008	23.40	23.41	1.000
5.85	5.75	0.983	11.70	12.02	1.027	23.40	23.67	1.012
5.85	6.02	1.029	11.70	11.52	0.985	23.40	24.46	1.045
5.85	5.97	1.021	11.70	11.42	0.976	23.40	23.23	0.993
5.85	5.92	1.012	11.70	11.44	0.978	23.40	24.69	1.055
n =		6			6			6
mean		1.025			0.995			1.019
std dev		0.0266			0.0197			0.0250
CV_1		0.0260			0.0198			0.0245

$\overline{CV}_1$ 0.0236

$\overline{CV}_{A+\overline{DE}}$ 0.0255

Table 3

Data Sheet: Triorthocresyl Phosphate, S209
(37-mm Type AA Millipore Filter)

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	3.300	101.2	0.0326
	2.779	100.9	0.0275
	2.857	100.5	0.0284
	2.655	101.1	0.0263
	2.888	100.8	0.0287
	3.317	101.6	0.0326
		n = 6	
		mean	0.0294
		std dev	0.00265
		CV_2	0.0902
1S	7.40	101.4	0.0730
	7.41	101.5	0.0730
	7.94	101.0	0.0786
	7.60	101.8	0.0747
	7.83	102.2	0.0766
	7.89	101.6	0.0777
		n = 6	
		mean	0.0756
		std dev	0.00240
		CV_2	0.0317
2S	16.25	101.4	0.1603
	15.15	101.2	0.1497
	17.89	101.3	0.1766
	18.31	101.2	0.1809
	18.24	101.0	0.1806
	17.38	102.1	0.1702
		n = 6	
		mean	0.1697
		std dev	0.01249
		CV_2	0.0736
		$\overline{CV}_2$	0.0697

Backup Data Report

Substance: Triphenyl phosphate, No. S210

OSHA Standard: 3.0 mg/cu m

Chemical used for Validation: Triphenyl phosphate, Aldrich Chemical, 98%

Procedure

The general procedure used is described in NIOSH Method No. S210 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 127 for the GC analysis of organic samples. The reliability of the analytical method was tested at sample concentrations equal to that present in a 100-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in ether was added to 37 mm Type AA Millipore filters. The analyte was extracted from the filter with ether and analyzed in a Varian 2700 Gas Chromatograph with a flame photometric detector and an auxiliary automatic sample injector, Varian Model 8000. A Spectra Physics System 1 Computing Integrator was used for area measurements and determination of sample concentration. A set of 18 generated samples, 6 at each of the 0.5, 1 and 2X the OSHA standard concentration, was collected and analyzed similarly. Details of the analytical procedure may be found in Section 8 of the NIOSH Method No. S210 and in the Butyl Acetate S47 Backup Data Report and attachment.

Modification

P&CAM 127 was modified to suit the needs for this particular analysis. A flame photometric detector with a phosphorus-filter was used for specificity and sensitivity and ether was substituted for carbon disulfide in order to minimize solvent interference.

Generation

Two methods of generating triphenyl phosphate atmospheres have been tried. Initially test atmosphere samples were generated by atomizing solutions of triphenyl phosphate in either ethyl acetate or isopropyl alcohol using the ERC Fluid Atomization Aerosol Generator Model 7330. This method of generation led to problems associated with poor collection efficiency on filters. It appears that the solvents may be altering the characteristics and porosity of the filter leading to poor collection efficiency. The poor collection efficiency is not due to the presence of triphenyl phosphate vapor because a set of controlled experiments run using filters spiked with 1280 micrograms of triphenyl phosphate showed no loss of triphenyl phosphate even after drawing 200 liters of air through the filters. Table 1 shows the data for a set of 8 spiked filters processed such that 4 filters served as controls while the other 4 were subjected to a flow of 200 liters of air at 1.5 liters per minute. The

generation problem was overcome by using neat triphenyl phosphate for generation.

TABLE 1

Data to Verify Volatility of Triphenyl Phosphate

µg Found	
Spiked Filters (Controls)	Spiked Filters and Air
1302	1295
1278	1275
1292	1311
1307	1298

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by direct atomization of liquified triphenyl phosphate. Approximately 380 g of triphenyl phosphate was added to a 500 ml three-neck round-bottom flask, and was heated to approximately 55°C (MP 49-50°C) with a heating mantle. The liquid was nebulized using a Laskin nozzle (Figure 1), with an orifice diameter of 0.012 inches and operated at a pressure of 13 psig. The air flow rate through the nebulizer was 0.5 liter per minute and the aerosol from the nebulizer was diluted with 146 liters per minute of dry air in a glass dilution tube (Figure 2) prior to entry into the mainline of the generation/dilution system described in detail in the S97 Octachloronaphthalene Backup Data Report and Attachment. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5X the OSHA standard level. All 6 samples at the 3 test levels were collected at 1.5 liters per minute for 66 minutes (100 liters); however, the complete set of 18 samples was not collected simultaneously. The 12 samples at the 0.5 and 1X OSHA standard level were collected simultaneously but the 6 samples at 2X OSHA standard level were collected on a different day.

Collection Efficiency

To determine the collection efficiency of the 37-mm Type AA Millipore filter for triphenyl phosphate aerosols, two filters were mounted in the three-piece filter cassette such that the front and backup filters were physically separated and only the backup filter was supported by the cellulose backup pad. Six such sample filter cassettes were used to determine the collection efficiency for an air sample concentration of 7.0 mg/cu m at a sampling rate of 1.5 liters per minute for 66 minutes. Each filter was analyzed separately and the relative amount of triphenyl phosphate collected in the primary and backup filters was determined, based on the total quantity found in both filters. The data summarized in Table 2 show that the average collection efficiency for triphenyl phosphate is 99.3%.

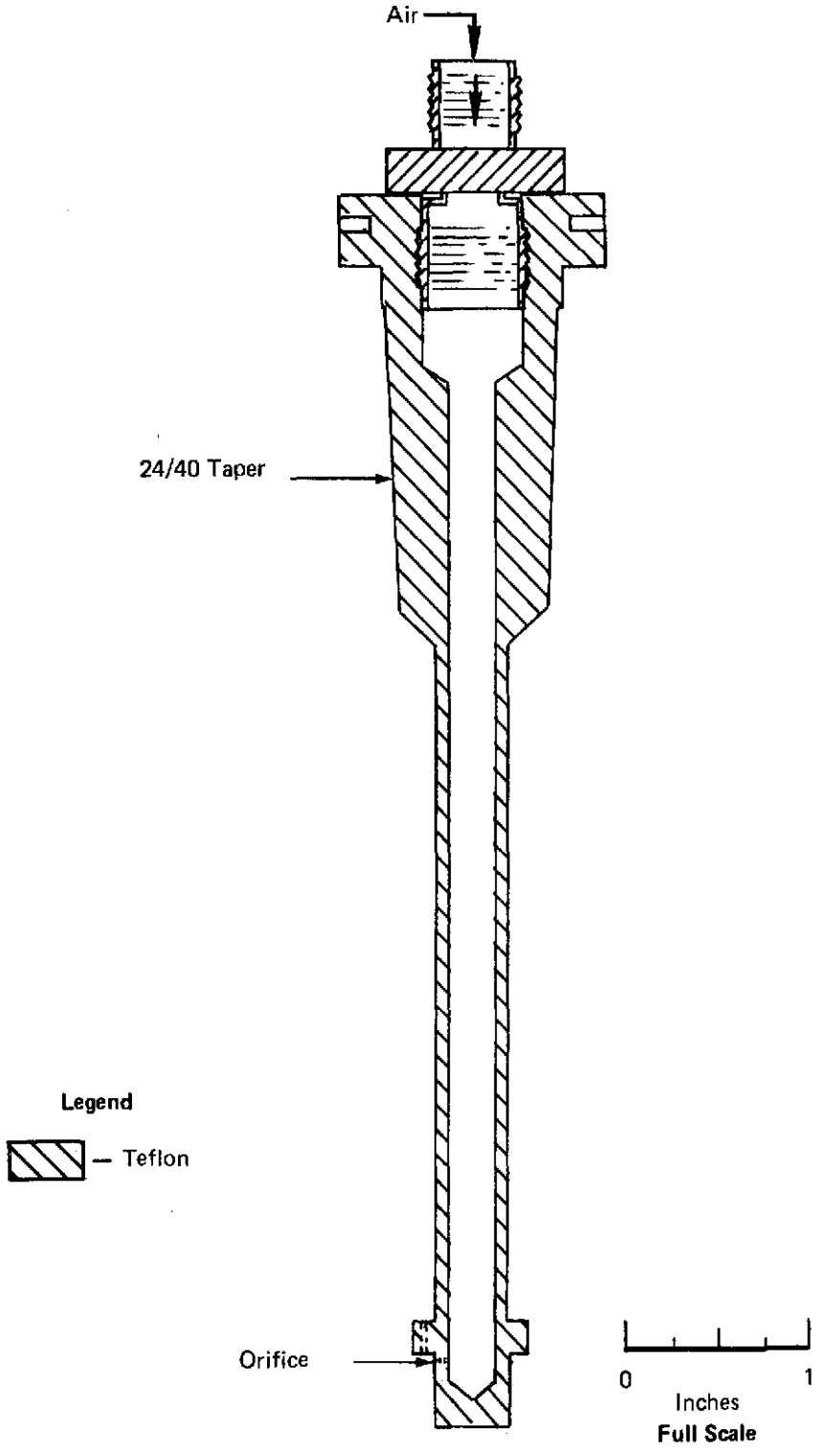

FIGURE 1 CROSS SECTIONAL VIEW OF LASKIN TYPE NOZZLE

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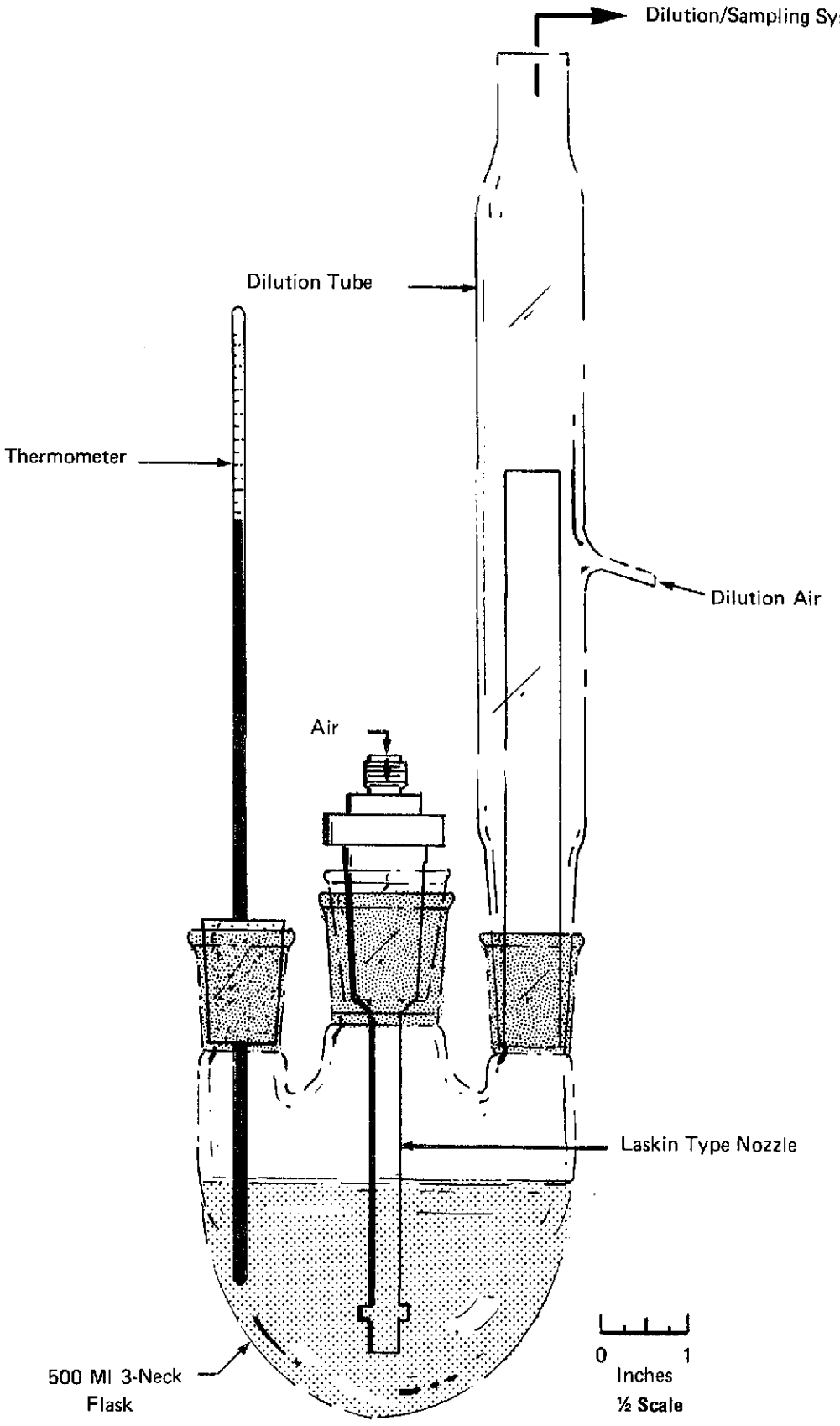

FIGURE 2 CROSS-SECTIONAL VIEW OF NEBULIZER/DILUTION SYSTEM

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TABLE 2

Collection Efficiency: Triphenyl Phosphate, S210

μg Found			
Front	Backup	Total	% Collected in Front
659	ND	659	100.0
669	ND	669	100.0
728	ND	728	100.0
775	ND	775	100.0
710	ND	710	100.0
680	30	710	95.8

Average Collection Efficiency..... 99.3%

ND - Not detectable; the lower limit of detection is 10 μg/10 ml.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0234$ $\overline{CV}_2 = 0.0420$ $\overline{CV}_T = 0.0660$

Reference

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

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TABLE 3

Data Sheet: Triphenyl phosphate, S210

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
150	145.7	0.971	303	303	1.000	606	593	0.979
150	149.8	0.999	303	300	0.990	606	617	1.018
150	152.1	1.014	303	303	1.000	606	603	0.995
150	148.5	0.990	303	301	0.993	606	600	0.990
150	145.5	0.970	303	303	1.000	606	588	0.970
150	153.3	1.022	303	310	1.023	606	560	0.924
n =		6			6			6
mean		0.994			1.001			0.979
std dev		0.0216			0.0116			0.0316
CV_1		0.0217			0.0116			0.0323

$\overline{CV}_1$ 0.0234

$\overline{CV}_{A+\overline{CE}}$ 0.0253

TABLE 4

Data Sheet: Triphenyl Phosphate, S210

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	120.0	99.5	1.206
	122.2	99.2	1.232
	127.1	98.8	1.286
	120.1	99.4	1.208
	125.9	99.1	1.270
	128.1	99.9	1.282
		n = 6	
		mean	1.247
		std dev	0.0366
		CV_2	0.0294
1S	280.5	99.7	2.813
	277.1	99.8	2.777
	292.8	99.3	2.949
	286.4	100.1	2.861
	289.8	100.5	2.884
	285.9	99.9	2.862
		n = 6	
		mean	2.858
		std dev	0.0593
		CV_2	0.0207
2S	659	100.7	6.54
	669	100.5	6.66
	728	100.6	7.24
	775	100.5	7.71
	710	100.3	7.08
	680	101.4	6.71
		n = 6	
		mean	6.99
		std dev	0.442
		CV_2	0.0633
		$\overline{CV}_2$	0.0420

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Backup Data Report

Substance: 1,1-Dichloro-1-nitroethane, No. S213

OSHA Standard: 60 mg/cu m

Chemical Used for Validation: 1,1-Dichloro-1-nitroethane, K&K Chemicals, 98%

Procedure

The general procedure used is described in NIOSH Method No. S213 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of 1,1-dichloro-1-nitroethane represented in a 17-liter air sample. To minimize errors associated with volume measurements of less than 1 microliter, a solution of 1,1-dichloro-1-nitroethane in carbon disulfide was used. The charcoal was Lot 104 activated petroleum-based charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

Activated petroleum-based charcoal, SKC Lot 104, was used instead of the coconut charcoal, SKC Lot 105, because the desorption efficiency from Lot 104 charcoal is higher; the DE were 0.95 and 0.37 from Lot 104 and Lot 105 respectively for 1.0 mg of analyte based on the analysis of duplicate samples for each charcoal type.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 11.62 mg/min of 1,1-dichloro-1-nitroethane via a syringe injector to a dry air stream flowing at a rate of 0.1014 cu m/min. The three sample lines were then maintained at dilution ratios of 0.240, 0.499 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 15 minutes (17 liters). The data reported is for the two sets of 18 samples collected; one set was stored for 1 day and the other set for 5 days in order to test sample stability. The average recovery obtained for the 1-day-old samples was 97.3% with $\overline{CV}_2 = 0.028$ while the 5-day-old samples yielded an average recovery of 99.7%, $\overline{CV}_2 = 0.017$. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 18 mg of 1,1-dichloro-1-nitroethane when a test atmosphere containing 116 mg/cu m of 1,1-dichloro-1-nitroethane in air was sampled at 0.79 liter per minute for 193 minutes; i.e., at that time the concentration of analyte in the effluent was 5% of that in the effluent.

Precision and Accuracy

The statistical procedures used are described in Reference 1 and coefficients of variation were calculated based on the data for the 5-day old samples.

$\overline{CV}_1 = 0.0379$ $\overline{CV}_2 = 0.0166$ $\overline{CV}_T = 0.0549$

The average recovery of the generated samples over all levels for the set stored for 5 days was 99.7%.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: 1,1-Dichloro-1-nitroethane, S213
(Lot 104/100 mg; Stored 5 days)

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.500	0.415	0.830	0.999	0.906	0.907	1.998	1.843	0.922
0.500	0.451	0.902	0.999	0.940	0.941	1.998	1.825	0.913
0.500	0.422	0.844	0.999	0.899	0.900	1.998	1.845	0.923
0.500	0.454	0.908	0.999	0.906	0.907	1.998	1.839	0.920
0.500	0.438	0.876	0.999	0.883	0.884	1.998	1.890	0.946
0.500	0.490	0.980	0.999	0.926	0.927	1.998	1.842	0.922
n =		6			6			6
mean		0.890			0.911			0.924
std dev		0.0538			0.0202			0.0112
CV_1		0.0605			0.0222			0.0121

$\overline{CV}_1$ 0.0379

$\overline{CV}_{A+\overline{DE}}$ 0.0409

Data Sheet: 1,1-Dichloro-1-nitroethane, S213
(Lot 104/100 mg; Sample Stored 1 Day)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.401	0.451	16.96	26.6	27.5	
	0.400	0.449	16.69	26.9	27.5	
	0.369	0.415	16.69	24.9	27.5	
	0.397	0.446	16.93	26.3	27.5	
	0.395	0.444	16.82	26.4	27.5	
	0.389	0.437	16.75	26.1	27.5	
			n = 6			
			mean	26.2		95.3
			std dev	0.693		
			CV_2	0.0264		
1S	0.813	0.903	16.85	53.6	57.2	
	0.812	0.902	16.94	53.2	57.2	
	0.868	0.964	17.16	56.2	57.2	
	0.792	0.880	16.99	51.8	57.2	
	0.834	0.927	16.84	55.0	57.2	
	0.842	0.936	16.85	55.5	57.2	
			n = 6			
			mean	54.2		94.8
			std dev	1.64		
			CV_2	0.0303		
2S	1.399*	1.521*	16.63	91.5*	114.5	
	1.754	1.907	16.58	115.0	114.5	
	1.756	1.909	16.81	113.6	114.5	
	1.770	1.924	16.88	114.0	114.5	
	1.866	2.028	16.87	120.2	114.5	
	1.836	1.996	16.69	119.6	114.5	
			n = 5			
			mean	116.5		101.7
			std dev	3.17		
			CV_2	0.0272		
			$\overline{CV}_2$	0.0281		

*These values excluded from statistical analysis

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Data Sheet: 1,1-Dichloro-1-nitroethane, S213
(Lot 104/100 mg; Sample Stored 5 Days)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.411	0.462	16.94	27.3	27.5	
	0.421	0.473	16.67	28.4	27.5	
	0.422	0.474	16.67	28.4	27.5	
	0.426	0.479	16.91	28.3	27.5	
	0.435	0.489	16.81	29.1	27.5	
	0.425	0.478	16.73	28.6	27.5	
			n = 6			
			mean	28.3		102.9
			std dev	0.589		
			CV_2	0.0208		
1S	0.855	0.950	16.84	56.4	57.2	
	0.848	0.942	16.93	55.6	57.2	
	0.893	0.992	17.14	57.9	57.2	
	0.843	0.937	16.97	55.2	57.2	
	0.860	0.956	16.82	56.8	57.2	
	0.865	0.961	16.84	57.1	57.2	
			n = 6			
			mean	56.5		98.8
			std dev	0.992		
			CV_2	0.0176		
2S	1.438*	1.564*	16.61	94.2*	114.6	
	1.708	1.857	16.57	112.1	114.6	
	1.719	1.868	16.79	111.3	114.6	
	1.723	1.873	16.87	111.0	114.6	
	1.743	1.895	16.85	112.5	114.6	
	1.703	1.851	16.67	111.0	114.6	
			n = 6			
			mean	111.6		97.4
			std dev	0.683		
			CV_2	0.0061		
			$\overline{CV}_2$	0.0166		

*These values excluded from statistical analysis

Backup Data Report

Substance: Ethylene glycol dinitrate and/or Nitroglycerin, No. S216

OSHA Standard: 0.2 ppm (1.0 mg/cu m), Ceiling

Chemical Used for Validation: Ethylene glycol dinitrate (83%) and nitroglycerin (17%) in ethyl alcohol - 10 g/100 ml and 1 g/100 ml

Nitroglycerin in ethyl alcohol - 5 mg/ml and 0.5 mg/ml

All of the above solutions were from Hercules, Inc.

Nitroglycerin Tablets, Eli Lilly and Co., manufactured for pharmaceutical use.

Procedure:

The general procedure used is described in NIOSH Method No. S216 which has been adopted from P&CAM 203. Desorption efficiency tests were done at 0.5, 1 and 2X the OSHA standard for a 15-liter sample by spiking with the appropriate aliquot of a solution of the analyte in ethyl alcohol. A set of 18 spiked samples, 6 at each of the 3 test levels, was prepared for ethylene glycol dinitrate and also for nitroglycerin. All samples were allowed to equilibrate at least overnight. The solid sorbent used for all studies was 100 mg of Tenax-GC resin, 35/60 mesh. Spiking and desorption tests were done in the 5-ml vials with Teflon-lined screw caps and the samples were desorbed with 2-ml of ethyl alcohol.

The samples were analyzed by gas chromatography using a Perkin-Elmer Model 900 Gas Chromatograph with a Ni-63 electron capture detector. The column was glass--2-1/2 ft x 1/4 inch, 2-mm I.D.--packed with 10% OV-17 on 60/80 mesh Gas Chrom Q. Initial tests indicated that the linear working range for ethylene glycol dinitrate was very limited and it was necessary to set up the analysis by diluting the sample solution obtained after desorption; a 1:5 dilution (i.e., 200 µl aliquot diluted to 1.0 ml with ethanol) was made for the analysis of ethylene glycol dinitrate. On the other hand, nitroglycerin has a wider linear range, and no further dilution was required for the analysis. The details of the analytical procedure may be found in the NIOSH Method No. S216. The appropriate DE correction factor used for the collected air samples was determined from the "hand drawn" DE curve based on the data shown in Table 1 for ethylene glycol dinitrate and in Table 2 for nitroglycerin.

Modification

There were no major modifications of P&CAM 203.

TABLE 1

Data Sheet: Ethylene glycol dinitrate, S216
(Tenax-GC/100 mg; Samples Stored for 1-8 Days)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
7.47	6.84	0.916	14.94	12.18	0.815	29.88	29.65	0.992
7.47	7.42	0.993	14.94	11.72	0.784	29.88	28.00	0.937
7.47	7.26	0.972	14.94	13.98	0.936	29.88	31.06	1.039
7.47	7.20	0.964	14.94	13.74	0.920	29.88	24.70	0.827
7.47	7.04	0.942	14.94	13.30	0.890	29.88	27.70	0.927
7.47	7.14	0.956	14.94	13.06	0.874	29.88	26.28	0.880
n =		6			6			6
mean		0.957			0.870			0.934
std dev		0.02637			0.0595			0.0759
CV_1		0.02755			0.0684			0.0813

$\overline{CV_1}$ 0.0634

$\overline{CV_{A+\overline{DE}}}$ 0.0684

TABLE 2

Data Sheet: Nitroglycerin, S216
(Tenax-GC/100 mg; Samples Stored for 2-7 Days)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
7.53	6.85	0.910	15.06	14.49	0.962	30.1	28.93	0.961
7.53	7.82	1.039	15.06	13.33	0.885	30.1	30.4	1.010
7.53	7.87	1.045	15.06	14.52	0.964	30.1	31.6	1.050
7.53	7.31	0.971	15.06	14.30	0.950	30.1	29.6	0.983
7.53	8.10	1.076	15.06	14.16	0.940	30.1	31.1	1.033
7.53	7.43	0.987	15.06	13.56	0.900	30.1	27.08	0.900
n =		6			6			6
mean		1.005			0.934			0.990
std dev		0.0605			0.0333			0.0545
CV_1		0.0602			0.0356			0.0550

$\overline{CV}_1$ 0.0514

$\overline{CV}_{A+\overline{DE}}$ 0.0555

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Generation

The generator used to produce test atmospheres of ethylene glycol dinitrate (EGDN) and nitroglycerin (NG) is shown schematically in Figure 1. The setup is a modified version of the vapor generation/dilution system described in the S47 Butyl Acetate Backup Data Report and Attachment; the syringe injector and delivery system has been replaced with the glass tower and needle valve arrangement. The glass tower was charged with Chromosorb P which had been dosed with a limited amount of ethylene glycol dinitrate or nitroglycerin. The main line air flow, maintained at 0.100 cu m/min, was split into two streams via the needle valve adjustment such that a small portion of the dry air stream was allowed to go through the glass tower prior to recombining with the rest of the main line stream; the needle valve was adjusted in order to produce the desired main line generator concentration equivalent to 2X OSHA standard test level.

For the generation of ethylene glycol dinitrate test atmospheres, 24 g of Chromosorb P was dosed with 2 g of ethylene glycol dinitrate using 25 ml of the stock solution (10 g/100 ml) containing both EGDN (83%) and NG (17%); the ethyl alcohol was evaporated off by air drying at room temperature. This batch of Chromosorb P with an EGDN and NG loading of 8.6% and 1.8% respectively was charged into the glass tower. At the air flow rate and temperature conditions used for this generation, only the EGDN was sufficiently vaporized to yield a test atmosphere containing 2X OSHA standard for EGDN; only trace amounts of nitroglycerin were observed in the collected samples.

In the case of nitroglycerin, generation of the test atmosphere at the desired concentration proved to be more difficult. The use of crushed nitroglycerin tablets mixed with Chromosorb P as described in Reference 1 was tried initially. This method was unsatisfactory because only low concentration levels of nitroglycerin could be produced in the dilution system. Attempts to increase the generator output by increasing the nitroglycerin loading on the Chromosorb from 0.1 to 0.5% NG by adding more of the crushed tablets or ethanolic extracts of the crushed tablets to weighed amounts of Chromosorb also proved unsuccessful. The test atmosphere concentration could not be sustained at a steady state even for a 1-hour period (i.e., the generator concentration drastically decreased with time) and test atmosphere concentrations greater than 1X OSHA standard could not be produced. For subsequent experiments, 15 g of Chromosorb P was loaded with 0.15 g of nitroglycerin using the 5 mg/ml solution of nitroglycerin in ethyl alcohol; the ethyl alcohol was evaporated by air drying. To facilitate vaporization, the glass tower was warmed very gently using heating tape wound around the tower.

Because of the low concentration levels required for this analyte, no independent method was available for assessing the generator concentration other than modifying the collection medium such as in the method used in Reference 1 using bubblers with ethanol for sample collection. For these validation studies, this secondary collection

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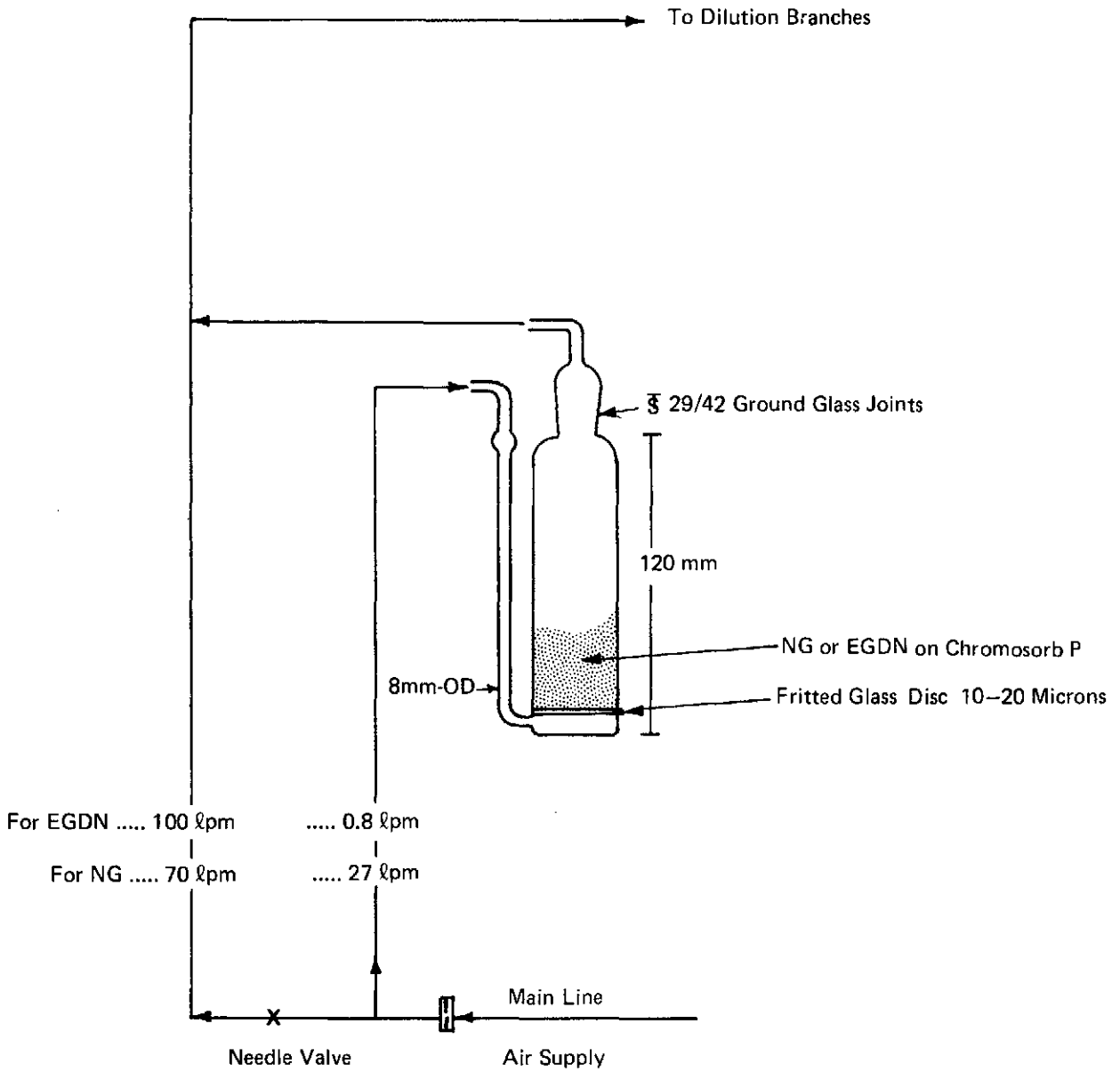

FIGURE 1 GENERATOR FOR NITROGLYCERIN AND ETHYLENE GLYCOL DINITRATE

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method was not used any more because the Reference 1 data conclusively proved that the Tenax-GC resin efficiently collected the nitrate esters at the prescribed sampling period and sampling rate. This is supported by the collection efficiency data on these two compounds shown in Tables 3 and 4. The collection efficiency was established as 100% and therefore the corrected "found" value is a measure of generator concentration.

The independent data for the collection and analysis of these two nitrate esters are shown in Tables 5 and 6 for 15-liter samples; the atmospheric temperature and pressure ranges for these studies were 22-24°C and 755-766 mm Hg.

Breakthrough

The capacity of the 100 mg of Tenax-GC for these two compounds was found to be:

(a) At least 0.4 mg of ethylene glycol dinitrate when a test atmosphere containing 1.6 mg/cu m of EGDN in air was sampled at 1.1 liters per minute for 240 minutes.

(b) At least 0.5 mg of nitroglycerin when a test atmosphere containing an average concentration of 2.7 mg/cu m of NG in air was sampled at 1.1 liters per minute for 240 minutes.

Breakthrough was not observed at that time, i.e., the concentration of the analyte in the effluent was less than 5% of that in the influent.

These values are based on the collection and analysis of the front and backup sections of duplicate samples for each compound at test concentrations equivalent to 2X OSHA standard; the duplicate samples were collected at interim periods of 60, 120 and 240 minutes as shown in Tables 3A and 4A. In addition, no ethylene glycol dinitrate or nitroglycerin was found in the backup sections of the six samples collected at 2X OSHA standard test level for each compound, Tables 3B and 4B.

Discussion

The nitrate ester samples are reported to be stable at room temperature on the Tenax-GC for at least 25 days (Reference 1) and was confirmed by studies on six samples spiked with 15 µg of EGDN and stored for 1 and 10 days. The average recovery for 3 samples stored for 10 days was 0.88 vs. 0.85 for the three 1-day-old samples. No further deliberate study on sample stability was conducted. However, the data shown in Tables 1 and 2 are for analytical samples stored and analyzed randomly over a one-week period for each of the two compounds. The samples were generally not analyzed in sets of six. The generated samples were also handled similarly and no independent data was obtained for freshly collected vs. stored samples.

TABLE 3

Collection Efficiency and Capacity of
Ethylene Glycol Dinitrate on Tenax-GC/100 mg

A. Samples collected for 60, 120, and 240 minutes at 1.1 liters per minute

μg Found			% Collected	Liters	Test Concentration
Front	Backup	Total	in Front	Collected	mg/cu m
77.2	0.06	77.26	99.9	64.8	1.192
88.4	0.05	88.45	99.9	64.6	1.369
178.5	0.04	178.54	100.0	127.3	1.403
183.5	0.04	183.54	100.0	130.3	1.409
406.2	19.75	425.95	95.4	255.6	1.666
387.7	8.23	395.93	97.9	259.2	1.528

B. Samples collected for 15 minutes at 1.1 liters per minute; Test Concentration = 1.84 mg/cu m

μg Found			% Collected
Front	Backup	Total	in Front
27.50	0.014	27.514	99.9
33.00	0.006	33.006	100.0
8.40	0.007	8.407*	99.9
30.70	0.006	30.706	100.0
27.91	0.010	27.920	100.0
30.90	0.008	30.908	100.0

Average Collection Efficiency . . . 100.0%

* This value is low probably due to a clogged orifice.

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TABLE 4

Collection Efficiency and Capacity of
Nitroglycerin on Tenax-GC/100 mg

A. Samples collected for 60, 120 and 240 minutes at 1.1 liters per minute

µg Found			% Collected	Liters	Test Concentration
Front	Backup	Total	in Front	Collected	mg/cu m
240.5	ND	240.5	100.0	70.2	3.43
236.5	ND	236.5	100.0	69.9	3.38
365.0	ND	365.0	100.0	129.3	2.82
346.0	ND	346.0	100.0	132.3	2.62
497.0	0.053	497.1	100.0	259.5	1.92
534.0	0.054	534.1	100.0	263.2	2.03

B. Samples collected for 15 minutes at 1.1 liters per minute; Test Concentration =

µg Found			% Collected
Front	Backup	Total	in Front
48.1	ND	48.1	100.0
50.4	ND	50.4	100.0
50.1	ND	50.1	100.0
54.7	ND	54.7	100.0
57.1	ND	57.1	100.0
55.4	ND	55.4	100.0

ND = Not detectable; the lower limit of detection for nitroglycerin was 0.04 µg/2 ml.

TABLE 5

Data Sheet: Ethylene glycol dinitrate, S216
(Tenax-GC/100 mg)

Sampling and Analysis

Test Level	Found			
	µg	Corr µg	Liters	mg/cu m
0.5S	7.83	8.51	16.32	0.521
	6.39	6.95	16.20	0.429
	8.05	8.75	16.27	0.538
	7.73	8.40	16.20	0.519
	7.79	8.47	16.39	0.517
	8.19	8.90	16.42	0.542
			n = 6	
			mean	0.511
			std dev	0.0415
			CV_2	0.0812
1S	13.94	15.15	15.87	0.955
	18.65	20.27	16.67	1.216*
	12.98	14.11	16.18	0.872
	14.37	15.62	16.30	0.958
	14.24	15.48	16.34	0.947
	14.62	15.89	16.29	0.976
			n = 5	
			mean	0.942
			std dev	0.0403
			CV_2	0.0428
2S	25.30	27.50	16.37	1.680
	30.40	33.00	16.30	2.025
	7.73	8.40	16.08	0.522*
	28.23	30.70	16.45	1.866
	25.68	27.91	16.14	1.729
	28.39	30.90	16.36	1.889
			n = 6	
			mean	1.838
			std dev	0.1371
			CV_2	0.0746
			$\overline{CV}_2$	0.0694

* These values excluded from statistical analysis

TABLE 6

Data Sheet: Nitroglycerin
(Tenax-GC/100 mg)

Sampling and Analysis

Test Level	Found			
	µg	Corr µg	Liters	mg/cu m
0.5S	6.97	7.14	15.85	0.450
	9.74	9.98	16.66	0.599
	9.39	9.62	16.17	0.595
	10.01	10.25	16.29	0.629
	8.38	8.58	16.33	0.525
	8.55	8.76	16.27	0.538
			n = 6	
			mean	0.556
			std dev	0.0651
			CV_2	0.117
1S	19.03	19.49	16.36	1.191
	18.95	19.41	16.29	1.192
	17.01	17.43	16.06	1.085
	17.83	18.27	16.44	1.111
	15.88	16.27	16.12	1.009
	16.45	16.85	16.35	1.031
			n = 6	
			mean	1.103
			std dev	0.0776
			CV_2	0.0703
2S	47.0	48.1	16.48	2.919
	49.2	50.4	16.41	3.07
	48.9	50.1	16.18	3.10
	53.4	54.7	16.56	3.30
	55.7	57.1	16.24	3.52
	54.1	55.4	16.47	3.36
			n = 6	
			mean	3.21
			std dev	0.2205
			CV_2	0.0687
			$\overline{CV}_2$	0.0882

The data shown in Table 5 for ethylene glycol dinitrate are for a complete set of 18 samples collected simultaneously. The data in Table 6 for nitroglycerin represent two separate experiments on generation and collection of the 18 samples, i.e., the 0.5S and 1S test levels were collected during one test run while the 2S test level was collected a few days later. This separate collection of the set of 18 samples was due to difficulties encountered in producing the required test concentration for nitroglycerin.

Precision and Accuracy

The statistical procedures used are described in Reference 2.

For ethylene glycol dinitrate

$\overline{CV}_1 = 0.0634$ $\overline{CV}_2 = 0.0694$ $\overline{CV}_T = 0.0893$

For nitroglycerin

$\overline{CV}_1 = 0.0514$ $\overline{CV}_2 = 0.0882$ $\overline{CV}_T = 0.1035$

Since the collection efficiency was found to be 100% for both compounds, and any analytical bias has been corrected by using the DE factor, $\overline{CV}_T$ is a satisfactory measure of accuracy.

References

1. Final Report for Contract No. HSM-99-73-63 to NIOSH, "Sampling and Analysis of Four Organic Compounds Using Solid Sorbents," Southern Research Institute, Birmingham, Alabama.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

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Backup Data Report

Substance:	Nitrobenzene, No. S217
OSHA Standard:	1 ppm (5 mg/cu m) - skin
Chemical Used for Validation:	Nitrobenzene, Lot 741158 Fisher Scientific Company

Procedure

The procedure for collecting and analyzing concentrations of nitrobenzene in air is described in NIOSH Method S217, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of nitrobenzene to represent 50-liter air samples. Samples of nitrobenzene were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with methanol and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for desorption efficiency (D.E.) to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 60 minutes). The "true" concentration at the 2X, 1X, and 0.5X OSHA standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were three major modifications to P&CAM 127.

1. The analyte was collected on 20/40 mesh silica gel instead of 20/40 mesh activated charcoal Lot 105. The analyte was collected in 7-cm long by 4-mm I.D. silica gel tubes containing 150 mg of silica gel in the adsorbing section and 75 mg in the backup section.

2. A solution of nitrobenzene in hexane, containing 60 mg/ml, was used to apply the analyte to the silica gel for desorption efficiency determinations. This was done so it would not be necessary to inject less than 2 µl at the 0.5X level.

3. Methanol was used as the eluent instead of carbon disulfide.

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* Silica gel tubes were obtained from Environmental Compliance Corp.

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Generation

Samples of nitrobenzene were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with nitrobenzene and placed in the syringe drive pump. The syringe, which was attached to a 15-inch long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 2.40 mg/minute. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.6 liters/minute and diluted with air at a rate of 192.9 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

Samples were collected for 60 minutes at a rate of approximately 0.930 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2 using the syringe drive pump and the same conditions described above. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 12.45 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.930 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

Preliminary desorption efficiency tests for nitrobenzene were conducted on charcoal Lot 105 at the 1X OSHA standard level. Four microliters of a stock solution containing 60 mg/ml of nitrobenzene in hexane was used to spike 100 mg of charcoal. Carbon disulfide, 95% ethanol, benzene, and methanol were tested as possible desorbing solvents. The samples were desorbed for 30 minutes and analyzed by gas chromatography. The GC conditions used were: 10 ft long X 1/8-in O.D. stainless steel column packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W; column temperature of 160°C; detector temperature of 275°C; injector temperature of 245°C. The results of the desorption efficiency trials are given below:

DESORPTION EFFICIENCY OF NITROBENZENE ON CHARCOAL LOT 105

Desorbing Solvent	mg taken	mg found	D.E.
Carbon Disulfide	0.2400	0.1178	0.491
95% Ethanol	0.2400	0.0816	0.340
Benzene	0.2400	0.1495	0.623
Methanol	0.2400	-0-	-0-

Because of the poor recovery of nitrobenzene on charcoal Lot 105, charcoal Lot 104 was tried, using carbon disulfide as the desorbing solvent. The samples were spiked as above, and the same GC conditions were used. Carbon disulfide gave an average recovery of nitrobenzene from charcoal Lot 104 of 0.565.

Silica gel (20/40 mesh) was tried to test the recovery of nitrobenzene using carbon disulfide and methanol as possible desorbing solvents. The same GC conditions as described above were used, and the same amount of stock solution of nitrobenzene was used to spike 150 mg of silica gel. The results are given below:

DESORPTION EFFICIENCY OF NITROBENZENE ON 20/40 MESH SILICA GEL

Desorbing Solvent	mg taken	mg found	D.E.
Carbon Disulfide	0.2400	0.0458	0.191
Methanol	0.2400	0.2376	0.990

From the above results, 20/40 mesh silica gel and methanol was used in the validation studies for nitrobenzene.

A time study was conducted to determine the recovery of nitrobenzene on silica gel when added from a vapor phase. Twelve samples at each of three levels were generated using the syringe drive pump as described under the Generation Section. Six samples at each level were used for the time study experiment. Three of the samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the silica gel tubes. The samples were allowed to stand for one week before analysis. The remaining six generated samples were analyzed immediately and the data are given in the Sampling and Analysis Table at the end of this report. The samples were desorbed with methanol for 30 minutes. The results are given below:

TIME STUDY RESULTS OF NITROBENZENE

	Found				Taken	
Level	mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
			(FLUSHED WITH NITROGEN)			
0.5X	0.169	0.169	55.8	3.03	3.11	
	0.164	0.164	54.1	3.03	3.11	
	0.160	0.160	55.4	2.89	3.11	
			mean	2.98		95.8
1X	0.316	0.315	56.7	5.56	6.22	
	0.329	0.328	52.2	6.28	6.22	
	0.331	0.330	56.3	5.86	6.22	
			mean	5.90		94.9
2X	0.714	0.713	55.4	12.87	12.45	
	Sample omitted due to malfunctioning orifice.					
	0.714	0.713	54.4	13.11	12.45	
			mean	12.99		104.3

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Level	Found mg found	Found corr. mg	Found Liters	Found mg/cu m	Taken mg/cu m	Recovery(%)
		(NOT FLUSHED WITH NITROGEN)				
0.5X	0.165	0.165	54.5	3.03	3.11	
	0.165	0.165	55.8	2.96	3.11	
	0.154	0.154	54.5	2.83	3.11	
			mean	2.94		94.5
1X	0.325	0.324	53.8	6.02	6.22	
	0.324	0.323	52.9	6.11	6.22	
	0.350	0.349	56.7	6.16	6.22	
			mean	6.10		98.1
2X	0.731	0.730	57.6	12.67	12.45	
	0.688	0.687	55.4	12.40	12.45	
	0.557	0.556	39.7	14.00	12.45	
			mean	13.02		104.6

An average desorption efficiency of 1.002 (calculated from Analysis table at the end of this report) was used to calculate corr. mg in the above table.

From the above results, nitrobenzene is stable on silica gel for at least one week without flushing with nitrogen. Comparison of these results with the data in the Sampling and Analysis data also show that nitrobenzene is stable for one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.010$ $\overline{CV}_2 = 0.029$ $\overline{CV}_T = 0.058$

The average recovery at the OSHA standard level was 99.4%.

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Nitrobenzene S217

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.1200	0.1202	1.002	0.2400	0.2386	0.994	0.480	0.485	1.010
0.1200	0.1228	1.023	0.2400	0.2358	0.982	0.480	0.477	0.994
0.1200	0.1206	1.005	0.2400	0.2409	1.004	0.480	0.480	1.000
0.1200	0.1181	0.984	0.2400	0.2408	1.003	0.480	0.481	1.002
0.1200	0.1210	1.008	0.2400	0.2410	1.004	0.480	0.480	1.000
0.1200	0.1218	1.015	0.2400	0.2392	0.997	0.480	0.483	1.006
n =		6			6			6
mean		1.006			0.997			1.002
std dev		0.013			0.009			0.006
CV_1		0.013			0.009			0.006

$\overline{CV}_1$ 0.010

$\overline{CV}_{A+\overline{DE}}$ 0.011

An average desorption efficiency (D.E.) of 1.002 was used to calculate corr. mg in the Sampling and Analysis table.

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Data Sheet: Nitrobenzene S217

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.1745	0.1742	55.8	3.12	3.11	
	0.1680	0.1677	54.5	3.08	3.11	
	0.1785	0.1781	54.1	3.29	3.11	
	0.1748	0.1745	55.4	3.15	3.11	
	0.1767	0.1764	55.8	3.16	3.11	
	0.1659	0.1656	54.5	3.04	3.11	
			n = 6			
			mean	3.14		101.0
			std dev	0.086		
			CV_2	0.027		
1S	0.340	0.339	56.7	5.98	6.22	
	0.330	0.329	53.8	6.12	6.22	
	0.330	0.329	52.9	6.22	6.22	
	0.358	0.357	56.7	6.30	6.22	
	0.337	0.336	52.2	6.44	6.22	
	0.341	0.340	56.3	6.04	6.22	
			n = 6			
			mean	6.18		99.4
			std dev	0.17		
			CV_2	0.028		
2S	0.734	0.733	55.4	13.23	12.45	
	0.758	0.756	57.6	13.12	12.45	
	0.723	0.722	55.4	13.03	12.45	
	0.706	0.705	55.4	12.73	12.45	
	0.552	0.551	39.7	13.88	12.45	
	Sample lost due to malfunctioning orifice.					
			n = 5			
			mean	13.20		106.0
			std dev	0.42		
$\overline{CV}_2$ 0.029			CV_2	0.032		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	p-Nitrochlorobenzene, No. S218
OSHA Standard:	1 mg/cu m - skin
Chemical Used for Validation:	p-Nitrochlorobenzene Aldrich

Procedure

The procedure for collecting and analyzing p-nitrochlorobenzene in air is described in NIOSH Method No. S218, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of p-nitrochlorobenzene to represent 50-liter air samples. Test atmospheres of p-nitrochlorobenzene were generated and samples collected in silica gel tubes. The analyte was desorbed with methanol and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for desorption efficiency (D.E.) to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 60 minutes). It was not possible to determine the "true" concentration in the generation system. However, it was possible to monitor the constancy of the concentration levels at the three OSHA standard levels using a total hydrocarbon analyzer.

Modifications

There were three major modifications to P&CAM 127.

1. The analyte was collected on 20/40 mesh silica gel instead of 20/40 mesh activated charcoal. The analyte was collected in 7-cm long by 4-mm I.D. silica gel tubes containing 150 mg of silica gel in the adsorbing section and 75 mg in the backup section.

2. A solution of p-nitrochlorobenzene in a benzene-hexane solution containing 12.5 mg/ml, was used to apply the analyte to the silica gel for desorption efficiency determinations.

3. Methanol was used as the eluent instead of carbon disulfide.

*Silica gel tubes were obtained from Environmental Compliance Corp.

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Generation

Samples of p-nitrochlorobenzene in air were generated using the two-piece vapor generator which is described in Reference No. 1. Solid p-nitrochlorobenzene was placed in the two-piece generator and heated to 40°C in a thermostatically controlled oil bath. Nitrogen was forced through the warm solid at 0.561 liter/minute. The p-nitrochlorobenzene vapor-nitrogen gas mixture was diluted with air at a flow rate of 182.5 liters/minute. The approximate concentration of p-nitrochlorobenzene in the sampling chamber was set as follows. A bag standard of chlorobenzene was prepared, and measured by hydrocarbon analyzer. An estimate was made of the hydrocarbon analyzer response which would be measured for the analyte at the 2X level, using the results of the bag standard as a guide. Nitrogen flow through the generator was adjusted until the concentration in the sampling chamber was at the selected level. Chlorobenzene was chosen for a standard because it is expected to give a similar response to the analyte, and because it is a liquid at room temperature so bag standards could easily be prepared. The generation conditions above resulted in concentrations lower than expected.

A second generation attempt was made by changing the nitrogen and the dilution air flow rates. The nitrogen flow rate was 5.14 liters/minute and the dilution air flow rate was 240 liters/minute. The concentrations in the three sampling chambers were again monitored with the total hydrocarbon analyzer, and the chlorobenzene bag standard used for comparison. These generation conditions gave concentrations of p-nitrochlorobenzene which were higher than expected.

Samples were collected in both generation attempts for 60 minutes at a rate of approximately 0.9 liter/minute.

Collection efficiency was determined to be 1.00, therefore the "true" and "found" concentrations were considered to be equal.

The 0.5X and 1X data were taken from the first generation attempt, and the 2X data were taken from the second generation attempt.

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2 using the same generation conditions as the second generation attempt. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 9.94 mg/cu m (as determined by analysis of samples taken) was present in the effluent after four hours at a rate of approximately 0.90 liter/minute, at which time the test was discontinued. Breakthrough was not observed.

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Collection Efficiency

Collection efficiency tests were conducted at a concentration of 2.75 mg/cu m by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00, since p-nitrochlorobenzene was not detected at a detection limit of 0.00125 mg/cu m.

Discussion

From our previous experience with poor recovery of nitrobenzene from charcoal Lot 105, recovery of p-nitrochlorobenzene from charcoal Lot 105 was not tested.

Preliminary desorption efficiency tests were conducted on 150-mg portions of 20/40 mesh silica gel and on 100-mg portions of charcoal Lot 104. The desorption efficiency tests were conducted at the 2X OSHA level using 8 µl of a stock solution of the analyte in a benzene-hexane solution (125 mg analyte/2 ml benzene and 8 ml hexane) for spiking. Carbon disulfide and methanol were tested as possible desorbing solvents. The samples were desorbed for one hour in an ultrasonic bath. The GC conditions used were 10-ft X 1/8-in. stainless steel column packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W; column temperature 155°C; detector temperature 260°C; injector temperature 180°C. The results of the D.E. trials are given below:

DESORPTION EFFICIENCY OF p-NITROCHLOROBENZENE
ON 20/40 MESH SILICA GEL

Desorbing Solvent	mg taken	mg found	D.E.
Carbon Disulfide	0.100	0.021	0.210
Carbon Disulfide	0.100	0.017	0.170
Carbon Disulfide	0.100	0.018	0.180
		mean	0.187
Methanol	0.100	0.100	1.00
Methanol	0.100	0.101	1.01
Methanol	0.100	0.106	1.06
		mean	1.02

DESORPTION EFFICIENCY OF p-NITROCHLOROBENZENE
ON CHARCOAL LOT 104

Desorbing Solvent	mg taken	mg found	D.E.
Carbon Disulfide	0.100	0.035	0.350
Carbon Disulfide	0.100	0.035	0.350
Carbon Disulfide	0.100	0.034	0.340
		mean	0.347
Methanol	0.100	-0-	-0-
Methanol	0.100	-0-	-0-
Methanol	0.100	-0-	-0-
		mean	-0-

From the above results, 20/40 mesh silica gel was chosen as the collection medium, and methanol was chosen as the desorbing solvent.

A time study was conducted by spiking 150-mg portions of 20/40 mesh silica gel at each of the three OSHA levels. Two, four, and eight microliters of the stock solution of p-nitrochlorobenzene in a benzene-hexane solution (12.5 mg/ml benzene-hexane) was used. The samples were stored for one week before analysis. The samples were desorbed with methanol for one hour in an ultrasonic bath and analyzed by GC, using the same GC conditions as described above. The results of the time study are given below:

TIME STUDY RESULTS OF p-NITROCHLOROBENZENE

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.025	0.025	1.000	0.050	0.058	1.160	0.100	0.105	1.050
0.025	0.023	0.920	0.050	0.054	1.080	0.100	0.105	1.050
0.025	0.025	1.000	0.050	0.048	0.960	0.100	0.103	1.030
0.025	0.026	1.040	0.050	0.053	1.060	0.100	0.103	1.030
0.025	0.026	1.040	0.050	0.052	1.040	0.100	0.100	1.000
0.025	0.025	1.000	0.050	0.054	1.080	0.100	0.105	1.050
n =		6			6			6
mean		1.000			1.063			1.035
std dev		0.044			0.065			0.020

The time study results were compared with the D.E. data in the Analysis Table at the end of this report. The D.E. data in the Analysis Table represents samples which were analyzed immediately. Based on these results, p-nitrochlorobenzene is stable on silica gel for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.025$ $\overline{CV}_2 = 0.089$ $\overline{CV}_T = 0.103$

Data Sheet: p-Nitrochlorobenzene S218

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.025	0.026	1.040	0.050	0.051	1.020	0.100	0.098	0.980
0.025	0.026	1.040	0.050	0.049	0.980	0.100	0.105	1.050
0.025	0.026	1.040	0.050	0.052	1.040	0.100	0.104	1.040
0.025	0.026	1.040	0.050	0.049	0.980	0.100	0.106	1.060
0.025	0.027	1.080	0.050	0.052	1.040	0.100	0.103	1.030
0.025	0.027	1.080	0.050	0.051	1.020	0.100	0.102	1.020
n =		6			6			6
mean		1.053			1.013			1.030
std dev		0.021			0.027			0.028
CV_1		0.020			0.027			0.027

$\overline{CV}_1$ 0.025

$\overline{CV}_{A+\overline{DE}}$ 0.027

An average desorption efficiency of 1.032 was used to calculate the corr. mg in the Sampling and Analysis Table.

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Data Sheet: p-Nitrochlorobenzene S218

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.020	0.019	51.0	0.373
	0.021	0.020	44.8	0.446
	0.023	0.022	48.2	0.456
	0.023	0.022	48.2	0.456
	0.022	0.021	44.0	0.477
	0.018	0.017	47.5	0.358
			n = 6	
			mean	0.428
			std dev	0.049
			CV_2	0.114
1S	0.052	0.050	48.0	1.042
	0.049	0.047	46.3	1.015
	0.052	0.050	50.5	0.990
	0.054	0.052	48.5	1.072
	0.050	0.048	49.6	0.968
	0.052	0.050	51.2	0.977
			n = 6	
			mean	1.011
			std dev	0.040
			CV_2	0.040
2S	0.132	0.128	55.6	2.302
	0.143	0.139	48.8	2.848
	0.152	0.147	52.6	2.795
	0.140	0.136	52.6	2.586
	0.148	0.143	48.0	2.979
	0.159	0.154	51.8	2.973
			n = 6	
			mean	2.747
			std dev	0.261
$\overline{CV}_2$ 0.089			CV_2	0.095

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: Nitrotoluene, No. S223

OSHA Standard: 5 ppm (30 mg/cu m) - skin

Chemical Used for Validation: o-Nitrotoluene Aldrich

Procedure

The procedure for collecting and analyzing concentrations of nitrotoluene in air is described in NIOSH Method S223, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of o-nitrotoluene to represent 20-liter air samples. Samples of o-nitrotoluene were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with methanol and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for desorption efficiency (D.E.) to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 110 minutes). The "true" concentration at the 2X, 1X, and 0.5X OSHA standard levels could not be determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. Therefore, collection efficiency was determined by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00 at a detection limit of 0.00075 mg. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were four major modifications to P&CAM 127.

1. The analyte was collected on 20/40 mesh silica gel instead of 20/40 mesh activated charcoal. The analyte was collected in 7-cm long by 4-mm I.D. silica gel tubes containing 150 mg of silica gel in the adsorbing section and 75 mg in the backup section.

2. A solution of o-nitrotoluene in hexane, containing 150 mg/ml, was used to apply the analyte to the silica gel for desorption efficiency determinations. This was done so it would not be necessary to inject less than 2 µl at the 0.5X level.

*Silica gel tubes were obtained from Environmental Compliance Corp.

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3. Methanol was used as the eluent instead of carbon disulfide.

4. An ultrasonic bath was used to aid desorption.

Generation

Samples of o-nitrotoluene were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with o-nitrotoluene and placed in the syringe drive pump. The syringe, which was attached to a 15-inch long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 2.31 mg/minute. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.1 liters/minute and diluted with air at a rate of 30.79 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

The concentration of the generated samples at each level was found to be lower than expected. It is assumed that the cause of the low values was due to a possible loss of the analyte in the generator. This being the case, the "true" concentration at the 2X, 1X, and 0.5X OSHA standard level could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates. Collection efficiency was determined to be 1.00. Therefore, the "found" and "true" concentrations were considered to be equal.

Samples were collected for 110 minutes at a rate of approximately 0.185 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2 using the syringe drive pump. A syringe drive pump was used to generate the analyte at a concentration of 52 mg/cu m (as determined by analyses of samples taken at the 2X level). A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 52 mg/cu m was present in the effluent after 256 minutes of sampling at a rate of approximately 0.185 liter/minute, at which time the test was discontinued. Breakthrough was not observed.

Collection Efficiency

Collection efficiency tests were conducted at a concentration of 58.2 mg/cu m by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00, since o-nitrotoluene was not detected at a detection limit of 0.00075 mg.

Discussion

Commercial mononitrotoluene consists of a mixture of three isomers. Approximately 60% is the ortho isomer, 38% is the para isomer, and 2% is the meta isomer. Ortho-nitrotoluene was used in the validation studies. Since desorption of o-nitrotoluene from silica gel with methanol is essentially 100% complete, high desorption efficiencies are to be expected for the other two isomers also, and this method is expected to be suitable for these. The Sampling and Analytical Method No. S223 instructs users to prepare individual desorption efficiency curves for each isomer detected in the sample.

From our previous experience with poor recovery of nitrobenzene from charcoal, recovery of o-nitrotoluene from charcoal was not tested.

Preliminary desorption efficiency tests were conducted on 150-mg portions of 20/40 mesh silica gel. The desorption efficiency tests were conducted at the 2X OSHA level using 8 µl of a stock solution of o-nitrotoluene in hexane (150 mg/ml) for spiking. Carbon disulfide and methanol were tested as possible desorbing solvents. The samples were desorbed for one hour in an ultrasonic bath. The GC conditions used were 10-ft long X 1/8-in. O.D. stainless steel column packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W; column temperature 90°C; detector temperature 250°C; injector temperature 150°C. The results of the desorption efficiency trials are given below:

DESORPTION EFFICIENCY OF NITROTOLUENE
ON 20/40 MESH SILICA GEL

Desorbing Solvent	mg taken	mg found	D.E.
Carbon Disulfide	1.200	0.252	0.210
Methanol	1.200	1.194	0.995

From the above results, methanol was chosen as the desorbing solvent.

A time study was conducted by spiking 150-mg portions of 20/40 mesh silica gel at each of the three levels. Two, four, and eight microliters of the stock solution of o-nitrotoluene in hexane (150 mg/ml) was used. The samples were stored for one week before analysis. The samples were analyzed as described above. The results of the time study tests are given below:

TIME STUDY RESULTS OF NITROTOLUENE

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.300	0.313	1.043	0.600	0.614	1.023	1.200	1.236	1.030
0.300	0.306	1.020	0.600	0.608	1.013	1.200	1.267	1.056
0.300	0.296	0.987	0.600	0.606	1.010	1.200	1.252	1.043
0.300	0.311	1.037	0.600	0.611	1.018	1.200	1.273	1.061
0.300	0.313	1.043	0.600	0.603	1.005	1.200	1.227	1.023
0.300	0.304	1.013	0.600	0.610	1.017	1.200	1.246	1.038
n =		6			6			6
mean		1.024			1.014			1.042
std dev		0.022			0.006			0.015

The time study results were compared with the D.E. data in the Analysis Table at the end of this report. The D.E. data in the Analysis Table represents samples which were analyzed immediately. Based on these results, o-nitrotoluene is stable on silica gel for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.025$ $\overline{CV}_2 = 0.035$ $\overline{CV}_T = 0.062$

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Data Sheet: Nitrotoluene S223

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.300	0.289	0.963	0.600	0.638	1.063	1.200	1.238	1.032
0.300	0.291	0.970	0.600	0.614	1.023	1.200	1.292	1.077
0.300	0.296	0.987	0.600	0.633	1.055	1.200	1.264	1.053
0.300	0.297	0.990	0.600	0.651	1.085	1.200	1.319	1.099
0.300	0.295	0.983	0.600	0.648	1.080	1.200	1.286	1.072
0.300	0.301	1.003	0.600	0.596	0.993	1.200	1.257	1.048
n =		6			6			6
mean		0.983			1.050			1.064
std dev		0.014			0.035			0.024
CV_1		0.014			0.033			0.023

$\overline{CV}_1$ 0.025

$\overline{CV}_{A+\overline{DE}}$ 0.027

The equation D.E. = $1.060 - e^{-8.64 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Nitrotoluene S223

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.241	0.258	22.65	11.39
	0.261	0.273	23.84	11.45
	0.261	0.273	24.67	11.07
	0.246	0.261	23.48	11.12
	0.251	0.265	22.77	11.64
	0.237	0.255	22.30	11.44
			n = 6	
			mean	11.35
			std dev	0.22
			CV_2	0.019
1S	0.559	0.531	20.76	25.58
	0.553	0.526	20.76	25.34
	0.502	0.479	18.26	26.23
	0.552	0.525	19.69	26.66
	0.571	0.542	19.45	27.87
	0.580	0.551	20.04	27.50
			n = 6	
			mean	26.53
			std dev	1.02
			CV_2	0.038
2S	1.385	1.307	22.30	58.6
	1.384	1.306	21.94	59.5
	1.398	1.319	21.94	60.1
	1.392	1.313	21.94	59.8
	1.322	1.247	21.58	57.8
	1.252	1.181	22.06	53.5
			n = 6	
			mean	58.2
			std dev	2.5
$\overline{CV}_2$ 0.035			CV_2	0.043

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387 (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Tetranitromethane, No. S224

OSHA Standard: 1 ppm (8 mg/cu m)

Chemical Used for Validation: Tetranitromethane, Aldrich Chemical Co., 98%

Procedure

Tetranitromethane was collected in ethyl acetate/impingers and analyzed by gas chromatography using an alkali-flame ionization detector. A glass column, 6 ft x 1/4 inch, 2 mm ID, packed with 3% OV-101 on 100/120 mesh Supelcoport AW-DMCS was used for the analysis. Note that stainless steel columns should not be used because tetranitromethane reportedly reacts with such metals as iron, copper, brass and zinc (Merck Index). The gas chromatograph used was a Varian Model 2100 equipped with an alkali-flame ionization detector.

The reliability of the analytical method was tested by analyzing a set of 18 spiked samples as described in detail in NIOSH Method S224. The spiked samples were prepared by adding tetranitromethane to 15 ml of ethyl acetate in the polyethylene bottles; the amount added was equivalent to that present in a 250-liter sample at 0.5, 1 and 2 times the OSHA standard. These samples were stored for 5 days prior to analysis.

Modification

The method described as NIOSH Method S224 was developed after initially testing the applicability of P&CAM 127 for this analyte. It was established that the standard flame ionization detector does not have adequate sensitivity for tetranitromethane at the concentration range of interest. Substitution of an alkali-flame ionization detector solved the sensitivity problem. It was also established that charcoal is not a suitable collection medium because the 0.4 mg of tetranitromethane added could not be recovered from 100 mg of charcoal Lot 105 by any of the selected solvents tried. The solvents tested were those compatible with an alkali-flame ionization detector (carbon disulfide is incompatible) such as ether, ethyl acetate, isopropanol and methanol. None of these solvents desorbed any measurable tetranitromethane from the charcoal even with the aid of ultrasonic agitation. It was also observed that in desorbing tetranitromethane from charcoal with methanol, a yellow solution was obtained. The color intensity increases with time and indicates the possibility of tetranitromethane decomposition.

The alternative approach of collection in impingers containing a solvent was subsequently investigated by determining the collection efficiency of tetranitromethane in isopropanol and ethyl acetate. The collection efficiency experiments were done by simultaneously

collecting six samples at the 2S sampling ports. In each case two impingers in series were used for collection and 250-liter samples were collected at 1-liter per minute. Three samples were collected in isopropanol and the other three in ethyl acetate. The data summarized in Table 1 show that ethyl acetate is a better collection medium than isopropyl alcohol; the average collection efficiencies were respectively 93% and 74%.

Additional tests were conducted to determine the stability of solutions of tetranitromethane in ethyl acetate. Because of some observations regarding discoloration of solutions, the stability test was designed to determine the effect, if any, of temperature and light. Eight solutions were prepared by adding 2.063 mg of tetranitromethane to 25 ml of ethyl acetate. Each of four sample flasks were wrapped in aluminum foil to minimize exposure to light and duplicate samples were stored as indicated in Table 2. These eight samples were analyzed on the first, fifth and seventh days. The data summarized in Table 2 show no significant effect of storage condition nor time on the tetranitromethane recovery.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by delivering 1.4 mg/min of tetranitromethane via a syringe injector to a dry air stream flowing at a rate of 0.104 cu m/min at 19°C and 763 mm Hg atmospheric temperature and pressure. The three sample lines were maintained at dilution ratios of 0.238, 0.492 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. Assuming no loss of tetranitromethane along the sampling lines, the calculated generator concentration at the three sample lines were 3.2, 6.6 and 13.5 mg/cu m. However, the experimental results consistently showed that 25% of the tetranitromethane fed into the sample generator lines was lost in the process despite attempts to pre-condition the generator by priming the chamber with a higher concentration of tetranitromethane for at least one hour and then equilibrating the system at the 2S test level for another hour before the actual sample collection was initiated. This loss is attributed to the previously noted reactivity of tetranitromethane with iron and other metals as well as rubber, i.e., some loss is bound to occur along the stainless steel arms of the generator. Thus, for this validation study, the "found" values were used as a measure of generator concentration. Note that the average value found for each of the three test levels were in the ratio of 0.236, 0.492 and 1.000; these values are in excellent agreement with the originally measured dilution ratios. All the data indicate that the sampling and analysis method as described is valid and that the constant loss observed is due to losses in the generator. It should also be noted that during the 4-hour sampling period the impingers had to be refilled with ethyl acetate every 30 minutes in order to maintain the ethyl acetate volume at 10-15 ml. Details of the sample generation/dilution system may be found in the Butyl Acetate S47 Backup Data Report.

TABLE 1

Comparison of Tetranitromethane Collection in
Isopropyl Alcohol vs. Ethyl Acetate

Sample Size: 250 liters at 1 liter per minute

	Solvent	mg Found			% Collection Efficiency	
		Front	Back	Total		
A.	Isopropanol	1.250	0.300	1.550	80.6	
		1.375	0.550	1.925	71.4	
		1.375	0.550	1.925	71.4	
		Average Collection Efficiency				74.5
B.	Ethyl Acetate	2.480	0.175	2.655	93.4	
		2.063	0.200	2.263	91.2	
		2.263	0.150	2.413	93.8	
		Average Collection Efficiency				92.8

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TABLE 2

Stability of Tetranitromethane in Ethyl Acetate

Amount Added: 2.063 mg in 25 ml ethyl acetate

Storage Condition	Sample Age: 1 Day mg Found	1 Day Recovery	5 Days mg Found	5 Days Recovery	7 Days mg Found	7 Days Recovery
Room Temperature	2.10	1.02	2.04	0.99	2.01	0.97
	1.98	0.96	2.03	0.98	2.01	0.97
Room Temperature, no light*	2.20	1.07	2.06	1.00	2.04	0.99
	2.14	1.04	2.06	1.00	2.04	0.99
Refrigerated	2.15	1.04	2.08	1.01	2.01	0.97
	2.05	0.99	2.06	1.00	2.04	0.99
Refrigerated, no light*	2.15	1.04	2.08	1.01	2.08	1.01
	2.00	0.97	2.08	1.01	2.15	1.04

* Flasks wrapped with aluminum foil.

Collection Efficiency

Collection efficiency tests were done for air sample concentrations of 11.5 mg/cu m at a sampling rate of 1.1 liters per minute for 230 minutes. Two impingers containing 15 ml of ethyl acetate were connected in series to each of the six sampling ports at the 2S test level. The contents of the front and backup impingers were analyzed separately. The amount of tetranitromethane in the front impinger relative to the total found in the front and backup impingers was used as a measure of collection efficiency. The data for six samples summarized in Table 3 show an average collection efficiency of 0.895 $\pm$0.010; this value was used as a correction factor in Table 5.

Precision and Accuracy

The statistical procedures used are described in Reference 1 and the data used for the statistical calculations are shown in Tables 4 and 5.

$\overline{CV}_1 = 0.0142$ $\overline{CV}_2 = 0.0572$ $\overline{CV}_T = 0.0762$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 3

Collection Efficiency: Tetranitromethane, S224

mg Found			% Collected
Front	Backup	Total	in front
2.062	0.232	2.294	89.9
2.662	0.320	2.982	89.3
2.500	0.302	2.802	89.2
2.538	0.352	2.890	87.8
2.512	0.285	2.797	89.8
2.688	0.268	2.956	90.9

Average Collection Efficiency .... 89.5 ± 1.0%

TABLE 4

Data Sheet: Tetranitromethane, S224

Analysis
(Samples Stored for 5 Days)

Level	0.5S		1S			2S		
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
1.011	0.975	0.964	2.022	1.975	0.977	4.04	4.01	0.993
1.011	0.938	0.928	2.022	1.938	0.958	4.04	4.04	1.000
1.011	0.975	0.964	2.022	1.975	0.977	4.04	4.04	1.000
1.011	0.950	0.940	2.022	1.950	0.964	4.04	4.01	0.993
1.011	0.975	0.964	2.022	1.988	0.983	4.04	4.01	0.993
1.011	0.975	0.964	2.022	2.038	1.008	4.04	4.01	0.993
n =		6			6			6
mean		0.954			0.978			0.995
std dev		0.0159			0.0175			0.0036
CV_1		0.0167			0.0178			0.0036

$\overline{CV}_1$ 0.0142

$\overline{CV}_{A+\overline{CE}}$ 0.0154

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TABLE 5

Data Sheet: Tetranitromethane, S224

Sampling and Analysis

Test Level	Found			
	mg	Corr mgΔ	Liters	mg/cu m
0.5S	0.662	0.740	254.8	2.904
	0.650	0.726	250.7	2.896
	0.600	0.670	250.7	2.634
	0.600	0.670	250.4	2.673
	0.575	0.642	252.8	2.540
	0.575	0.642	251.6	2.552
			n = 6	
			mean	2.700
			std dev	0.163
			CV_2	0.0603
1S	1.225	1.369	253.2	5.41
	1.375	1.536	254.6	6.03
	1.200	1.341	257.8	5.20
	1.225	1.369	255.3	5.36
	1.375	1.536	253.0	6.07
	1.288	1.439	253.2	5.68
			n = 6	
			mean	5.63
			std dev	0.364
			CV_2	0.0646
2S	2.002*	2.237*	253.2	8.83*
	2.662	2.974	249.1	11.94
	2.500	2.793	252.5	11.06
	2.538	2.836	253.7	11.18
	2.512	2.807	253.4	11.08
	2.688	3.003	250.7	11.98
			n = 6	
			mean	11.45
			std dev	0.470
			CV_2	0.0410
			$\overline{CV}_2$	0.0572

*These values excluded from statistical analysis
ΔCorrected for collection efficiency factor = 0.895.

Backup Data Report

Substance:	Tetryl, No. S225
OSHA Standard:	1.5 mg/cu m - skin
Chemical Used for Validation:	Tetryl Received from test site at Coyote Point from the U.S. Army. The purity of tetryl was confirmed by performing a melting point test.

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S225, which has been adapted from the method described in Reference No. 1. Standard samples were prepared (from a benzene solution of tetryl containing 15 mg/ml), and a standard curve was constructed by plotting absorbance vs. μg of tetryl.

The reliability of the analytical method was tested at concentrations approximately equal to that present in a 100-liter air sample at 0.5X, 1X, and 2X the OSHA standard. Six samples were prepared at the three OSHA levels by spiking 5, 10, and 20 microliters respectively of a benzene solution of tetryl (15 mg/ml) onto 37-mm/0.8-micron type AA MCEF filters. The filters were extracted with N,N-diethylethanolamine, and the samples were analyzed at 420 nm on a spectrophotometer. The amount of tetryl recovered from the filters were determined from the standard curve. This procedure was also used for the analysis of 18 generated samples, six at each of the three standard levels. Details of the analytical procedure may be found in Section 8.4 of NIOSH Method S225. Details of the generation of the analyte at the three concentration levels at approximately 0.5X, 1X, and 2X the OSHA standard are given below.

Modification

There were no major modifications of the method described in Reference No. 1.

Generation

Samples of tetryl particulate were generated by the fluid atomization technique described in Reference No. 2 and collected on 37-mm MCEF filters. A 0.5% weight/volume solution of tetryl in toluene was aspirated at a rate of 21 liters/minute to produce the aerosol droplets. Previous experiments involving microscopic examination of ammonium fluorescein particulate collected on 0.2-micron Nucleopore filters showed that a 0.5% weight/volume solution of tetryl in toluene should give particles with a mean diameter of approximately 1.1 micron.

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The liquid droplets were spray dried with 288 liters/minute of air to give a concentration of 4.51 mg/cu m at the 2X level. Appropriate amounts of dilution air were added to give a 1X concentration of 2.00 mg/cu m and a 0.5X concentration of 0.882 mg/cu m. The dilution system is described in Reference No. 3. The concentration in the generator was monitored by a Thermo-Systems Model 3200A particle mass monitor in conjunction with a Monsanto Model 103A counter/timer (Reference No. 4). The particle mass monitor allows for calibration of the generation system and for monitoring the concentration at all three levels during sample collection.

Samples were collected for 70 minutes at a rate of approximately 1.4 liters/minute.

Collection Efficiency

Collection efficiency at a concentration of 4.51 mg/cu m was determined by measuring the amount of particulate collected on each of the two filters in series mounted in direct contact with each other. The results of the collection efficiency tests are presented below.

mg/cu m First Filter	mg/cu m Backup Filter	Collection Efficiency
4.48	0.063	0.986
4.53	0.069	0.985
4.53	0.091	0.980
4.45	0.045	0.990
4.56	0.072	0.984
	mean	0.985
	std dev	0.004

From the above results, no correction for collection efficiency was needed.

Discussion

Preliminary work on tetryl using the particle mass monitor described in Reference No. 4 was conducted to determine if tetryl existed as a particulate, vapor, or both. The particle mass monitor was connected to the 2X sampling chamber during sample collection. After a period of 10 minutes, the particle mass monitor was disconnected from the 2X chamber, and clean filtered air was sampled through the particle mass monitor for a 0.5 hour. If tetryl had a significant vapor pressure, particulate matter would have vaporized off of the crystal resulting in a decrease in the frequency shift shown on the counter/timer. No such change was noted; therefore, tetryl was expected to exist totally as a particulate at ambient conditions.

A time study at the 1X level was conducted by spiking six 37-mm MCEF filters with 10 microliters of a benzene solution of tetryl (15 mg/ml). The samples were allowed to stand for six days before analysis. The results are presented below:

µg taken	µg found	A.M.R.
150.0	150.4	1.003
150.0	153.8	1.025
150.0	150.1	1.001
150.0	155.3	1.035
150.0	150.7	1.005
150.0	151.6	1.011
	mean	1.013
	std dev	0.014

These results were compared with the immediately analyzed 1X A.M.R.'s in the Analysis Table. It was concluded that tetryl is stable for at least six days.

Precision and Accuracy

The statistical procedures used are described in Reference No. 5.

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for tetryl as in Reference No. 6.

The sampling and analysis data gave chi squared value of 12.2, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01.

The data for tetryl show excellent precision. Therefore, pooling will not introduce significant error. For this reason, $\overline{CV}_T$ is calculated on all the data.

$\overline{CV}_1 = 0.038$ $\overline{CV}_2 = 0.039$ $\overline{CV}_T = 0.065$

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Data Sheet: Tetryl S225

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
75.0	74.6	0.995	150.0	146.7	0.978	300.0	296.3	0.988
75.0	74.6	0.995	150.0	148.5	0.990	300.0	284.5	0.948
75.0	79.0	1.053	150.0	147.0	0.980	300.0	285.1	0.950
75.0	75.0	1.000	150.0	142.3	0.949	300.0	282.7	0.942
75.0	85.2	1.136	150.0	142.6	0.951	300.0	283.9	0.946
75.0	72.5	0.967	150.0	147.6	0.984	300.0	280.2	0.934
n =		6			6			6
mean		1.024			0.972			0.951
std dev		0.061			0.018			0.019
CV_1		0.060			0.019			0.020

$\overline{CV}_1$ 0.038

$\overline{CV}_{A+\overline{AMR}}$ 0.041

The average Analytical Method Recovery (A.M.R.) at each level was used to calculate the corr. µg at each level in the Sampling and Analysis Table.

Data Sheet: Tetryl S225

Sampling and Analysis

Test Level	Found			
	µg	Corr. µg	Liters	mg/cu m*
0.5S	91.6	89.5	101.2	0.884
	91.3	89.2	103.7	0.860
	92.0	89.8	102.4	0.877
	85.1	83.1	102.4	0.812
	91.6	89.5	101.2	0.884
	102.2	99.8	102.4	0.975
			n = 6	
			mean	0.882
			std dev	0.053
			CV_2	0.060
1S	198.3	204.0	105.0	1.943
	192.4	197.9	100.0	1.979
	193.0	198.6	100.0	1.986
	196.4	202.1	98.8	2.046
	196.1	201.8	97.7	2.066
	192.7	198.3	100.0	1.983
			n = 6	
			mean	2.000
			std dev	0.046
			CV_2	0.023
2S	453	476	106.3	4.48
	458	482	106.3	4.53
	453	476	105.0	4.53
	445	468	105.0	4.45
	418	440	96.5	4.56
	377	396	98.8	4.01*
			n = 5	
			mean	4.51
			std dev	0.04
$\overline{CV}_2$	0.039		CV_2	0.009

* Deleted as an outlier because this value did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 7.

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References

1. Goldman, F. H. and D. E. Rushing, "The Estimation of Minute Amounts of Tetryl in the Atmosphere," Journal of Industrial Hygiene and Toxicology, 25 (5), (1943), 195.

2. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Trichloronaphthalene, No. S128, prepared under NIOSH Contract CDC-99-74-45.

5. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

6. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

7. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: n-Propylnitrate, S227

OSHA Standard: 110 mg/cu m

Chemical Used for Validation: n-Propylnitrate, Aldrich, 97%

Procedure

The general procedure used is described in NIOSH Method No. S227 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of n-propylnitrate represented in a 70-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using decane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 20.6 mg/min of n-propylnitrate via a syringe injector to a dry air stream flowing at a rate of 0.0987 cu m/min. The three sample lines were then maintained at dilution ratios of 0.240, 0.499 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 64 minutes (70 liters). A sample size of 70 liters was used on the basis of the two-thirds breakthrough capacity. The data reported is for the two sets of 18 samples collected; the first set was stored for 1 day while the second set was stored for 5 days in order to test sample stability. The average recovery obtained for the 1-day-old samples was 91.7% with $\overline{CV}_2$ = 0.064 while the 5-day-old samples yielded an average recovery of 100%, $\overline{CV}_2$ = 0.019. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 24 mg of n-propylnitrate when a test atmosphere containing 209 mg/cu m of n-propylnitrate in air was sampled at 0.79 liters per minute for 143 minutes; i.e., at that time the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0127$ $\overline{CV}_2 = 0.0187$ $\overline{CV}_T = 0.0536$

The average recovery of the generated samples over all levels for the sample stored for 5 days was 100.4%.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: n-Propylnitrate, S227
(Lot 105/100 mg; Stored 1 day)

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.28	2.887	0.880	6.56	6.25	0.953	13.23	12.37	0.935
3.28	2.946	0.898	6.56	6.13	0.934	13.23	12.77	0.965
3.28	2.913	0.888	6.56	6.20	0.945	13.23	12.59	0.952
3.28	2.888	0.880	6.56	6.28	0.957	13.23	12.71	0.961
3.28	2.962	0.903	6.56	6.26	0.954	13.23	12.93	0.977
3.28	2.958	0.902	6.56	6.33	0.965	13.23	12.69	0.959
n =		6			6			6
mean		0.892			0.951			0.958
std dev		0.0106			0.0107			0.0140
CV_1		0.0119			0.0112			0.0146

$\overline{CV}_1$ 0.0127

$\overline{CV}_{A+\overline{DE}}$ 0.0137

Data Sheet: n-Propylnitrate, S227
(Lot 105/100 mg; Sample Stored 1 day)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.814	3.14	66.9	46.9	51.5	
	2.845	3.18	65.9	48.3	51.5	
	2.859	3.19	65.9	48.4	51.5	
	2.937	3.28	66.8	49.1	51.5	
	2.895	3.23	66.4	48.6	51.5	
	2.760	3.08	66.1	46.6	51.5	
			n = 6			
			mean	48.0		93.2
			std dev	0.999		
			CV_2	0.0208		
1S	6.42	6.79	66.5	102.1	107.0	
	6.30	6.67	66.9	99.7	107.0	
	6.60	6.98	67.7	103.1	107.0	
	6.17	6.53	67.1	97.3	107.0	
	6.43	6.80	66.5	102.3	107.0	
	6.23	6.59	66.5	99.1	107.0	
			n = 6			
			mean	100.6		94.0
			std dev	2.25		
			CV_2	0.0224		
2S	10.17	10.59	65.6	161.4	214.5	
	13.10	13.65	65.5	208.4	214.5	
	13.52	14.08	66.3	212.4	214.5	
	12.47	12.99	66.6	195.0	214.5	
	11.36	11.83	66.6	177.6	214.5	
	11.11	11.57	65.9	175.6	214.5	
			n = 6			
			mean	188.4		87.8
			std dev	20.14		
			CV_2	0.1069		
			$\overline{CV}_2$	0.0642		

Data Sheet: n-Propylnitrate, S227
(Lot 105/100 mg; Sample Stored 5 Days)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.20	3.54	70.4	50.3	50.1	
	3.22	3.56	69.2	51.4	50.1	
	3.22	3.56	69.2	51.4	50.1	
	3.27	3.61	70.2	51.4	50.1	
	3.31	3.66	69.8	52.4	50.1	
	3.24	3.58	69.5	51.5	50.1	
			n = 6			
			mean	51.4		102.6
			std dev	0.666		
			CV_2	0.0130		
1S	6.88	7.24	69.9	103.6	104.2	
	7.00	7.37	70.3	104.8	104.2	
	7.26	7.64	71.2	107.3	104.2	
	6.69	7.04	70.5	99.9	104.2	
	7.05	7.42	69.9	106.2	104.2	
	7.06	7.43	69.9	106.3	104.2	
			n = 6			
			mean	104.7		100.5
			std dev	2.68		
			CV_2	0.0256		
2S	10.88*	11.28*	69.0	163.5*	208.8	
	13.46	13.95	68.8	202.8	208.8	
	13.92	14.42	69.7	206.9	208.8	
	13.63	14.12	70.1	201.4	208.8	
	13.93	14.44	70.0	206.3	208.8	
	13.89	14.39	69.2	207.9	208.8	
			n = 5			
			mean	205.1		98.2
			std dev	2.81		
			CV_2	0.0137		
			$\overline{CV}_2$	0.0187		

*These values excluded from statistical analysis

Backup Data Report

Substance: Arsine, No. S229

OSHA Standard: 0.2 mg/cu m

Chemical Used for Validation: Arsine in Nitrogen (14 ppm), Linde Specialty Gases

Procedure

The general procedure used is described in NIOSH Method No. S229. The collection method has been adapted from P&CAM 127. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Desorption efficiency tests have not been carried out because the low concentration of the arsine source would require that large volumes of gas (200-800 ml) had to be injected directly into the charcoal tube. The arsine vapor samples were collected using the sample collection equipment described in the Butyl Acetate S47 Backup Data Report. The samples were desorbed in 10.0 ml of 0.01 M nitric acid with ultrasonic agitation for 10-15 minutes. The samples were than allowed to stand for one hour with occasional shaking. Tests indicate that this desorption period is sufficient for adequate desorption.

The samples were analyzed in a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 503, equipped with a heated graphite atomizer, HGA Model 2100, and a Deuterium Background Corrector. A Hewlett Packard Recorder, Model 17501A was used. The source was an Electrodeless Discharge Lamp powered by a Perkin-Elmer EDL power supply. The arsenic absorption line at 193.7 nm was used for the assay.

With the aid of an Eppendorff automatic pipettor with disposable plastic tips, duplicate 50 microliter aliquots of the desorbed sample solutions were injected directly into selected graphite tubes. Argon was used as the inert gas stream flowing through the furnace. The furnace conditions were as follows:

Sample Cycle	Time in Seconds	Temperature, °C
Sample drying	40	150
Sample charring	20	250
Sample atomization	10	2200

Peak areas of the absorption peaks, as determined using the Perkin-Elmer 503 integrator accessory, were used to determine the quantity of arsenic present in the sample. The analyses were carried out such that the samples were carefully alternated with standards of about the same response as the sample in order to minimize errors due to observed instrument response variations.

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Discussion

The development of an analytical and sampling method for arsine was initiated by testing the arsine evolution method using the Perkin-Elmer Arsine Generator and sodium borohydride as reducing agent; the atomic absorption was measured at 193.7 nm. The reproducibility of calibration standards was studied from 0.1 to 1.0 µg of arsenic; poor precision was observed with a relative standard deviation of 15.6% over that concentration range. The precision was also tested for the 18-sample analytical set over a fourfold concentration interval by adding 0.2, 0.4, and 0.8 µg of arsenic as sodium arsenate into the generator. As shown in Table 1, the observed poor precision does not favor the use of this method; the relative standard deviation was 9.7%.

The alternative approach studied is the heated graphite atomizer (HGA) method for the analytical measurement of arsine; the absorbance at 193.7 nm was used. Initial analytical studies were done by considering both silver nitrate/impingers and charcoal tubes as viable routes for collection.

The HGA studies were initiated by testing the effect of silver nitrate concentration on the analytical scheme. It was observed that high concentrations of silver nitrate interferes with the assay because of the dense smoke formed during the ignition process, but a 0.01 M solution of silver nitrate was acceptable. Six analytical samples were prepared by adding 2 µg of arsenic (as sodium arsenate) into 10 ml of 0.01 M silver nitrate. This concentration is equivalent to a 10-liter sample at the OSHA standard level. Duplicate 50 µl aliquots of these six samples were analyzed by the HGA method. The data summarized in Table 2 indicate that poor precision was obtained when peak height measurements were used, but the precision was improved considerably when some form of peak area measurement was used. The relative standard deviation was 0.293 for peak height determined concentrations but dropped to 0.033 when the planimeter-integrated areas were used.

Subsequent studies were done using the Model 503 integrator accessory in the 10-second integration mode; the peak width of the absorption peaks was 3-5 seconds. Five calibration solutions containing 6-44 µg As/10 ml (3-22 nanograms/50 microliters) were analyzed repetitively six times and the observed relative standard deviation over this concentration interval was 2.7%

To test the precision of the method, eighteen samples were prepared by spiking 10 ml of 0.01 M silver nitrate with sodium arsenate containing arsenic equivalent to that present in a 10-liter sample at 0.5, 1, and 2X OSHA standard for arsine. The data summarized in Table 3 show an average recovery of 99.5% with $\overline{CV}_1 = 0.065$, indicating that the HGA method is acceptable.

Table 1

Arsine by Arsine Evolution

Perkin Elmer Arsine Generator: AA at 193.7 nm

Test on Reproducibility of Calibration Standards

µg Added	0.2	0.4	0.8
	µg Found		
	0.21	0.42	0.84
	0.17	0.40	0.73
	0.24	0.34	0.79
	0.23	0.44	0.74
	0.22	0.40	0.82
	0.20	0.42	0.67
mean	0.21	0.40	0.77
std dev	0.025	0.034	0.063
CV	0.118	0.086	0.082

$\overline{CV} = 0.097$

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Table 2

Arsine as Arsenic by HGA

Analytical Data in 0.01 M $AgNO_3$

Peak Height vs Peak Area

µg Added		µg Found	
		By Peak Height	By Peak Area[1]
2.0		2.06	1.99
2.0		3.58	2.03
2.0		2.04	2.06
2.0		3.62	2.09
2.0		1.98	1.90
2.0		2.54	2.01
	mean	2.64	2.01
	std dev	0.77	0.066
	CV_1	0.293	0.033

[1] Peak area determined by planimeter integration of areas of absorption peak. Recorder chart speed was run at fast mode .. i.e., 1 inch per second.

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Table 3

Data Sheet: Arsine$^{\Delta}$, S229
(10 ml 0.01 M Silver Nitrate)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
1.0	1.14	1.14	2.0	1.96	0.98	4.0	3.92	0.980
1.0	1.84	1.84*	2.0	1.80	0.90	4.0	3.98	0.995
1.0	0.90	0.90	2.0	2.06	1.03	4.0	3.84	0.960
1.0	1.00	1.00	2.0	2.02	1.01	4.0	4.26	1.065
1.0	0.92	0.92	2.0	1.98	0.99	4.0	4.32	1.080
1.0	0.96	0.96	2.0	1.94	0.97	4.0	4.16	1.040
n =	5			6			6	
mean		0.984			0.980			1.020
std dev		0.095			0.045			0.049
CV_1		0.097			0.046			0.048

$\overline{CV}_1$ 0.0651

$\overline{CV}_{A+\overline{DE}}$ 0.0705

* These values excluded from statistical analysis

Δ Samples spiked with sodium arsenate containing arsenic equivalent to 10 liters at 0.5, 1 and 2X OSHA standard for arsine.

In order to determine the most suitable collection media, a "quick-screening" process was set up using a single stage, six outlet miniature generator to test a series of alternative collection media for arsine. The experimental results summarized in Table 4 indicated that 0.1M silver nitrate and charcoal could both be acceptable. Further studies were conducted to evaluate both silver nitrate and charcoal for collection. The recommended method is collection on charcoal and desorption with 0.01 M nitric acid; the experimental data with silver nitrate is also presented, to indicate that the overall recovery with this method is low.

The collection efficiency in 10 ml of 0.1 M silver nitrate is 91%, as shown in Table 5 for a 110-liter sample. The solutions were diluted to 100 ml with 0.01 M nitric acid prior to analysis to decrease the silver nitrate concentration to 0.01 M. Two sets of 18 samples were collected--one set was analyzed immediately while the other set was stored for six days. The experimental results tabulated in Tables 6 and 7 show an average recovery of 89% for the fresh samples and 86% for the stored samples with a precision ($\overline{CV}_2$) of 0.066 and 0.038 respectively. All data have been corrected for a desorption efficiency of 0.91.

Generation

The test atmosphere samples at 0.5, 1 and 2X OSHA standard were generated by delivering arsine from a gas cylinder via a needle valve into the vapor generation equipment described in the Butyl Acetate S47 Backup Data Report. The arsine source is a mixture of arsine in nitrogen with a manufacturer's reported concentration of 14 ppm. The arsine content of the tank was independently calibrated by using the silver diethyldithiocarbamate/pyridine method described in P&CAM 140 and also by collection in 0.1 M silver nitrate and analysis by HGA. In both cases, known volumes of arsine from the gas cylinder were collected directly into either of the two collection media referred to above; the volume of arsine gas collected was determined by water displacement. The determined arsine concentration of the gas cylinder by the silver diethyldithiocarbamate method and by the silver nitrate/HGA method was 16.5 ppm and 15.8 ppm respectively. The generator concentration was calculated on the basis of the silver nitrate/HGA assay because this method appeared to be more reliable than the silver diethyldithiocarbamate method. The latter method required the preparation of a calibration curve by generating arsine by the action of metallic zinc on trivalent arsenic and absorbing the arsine formed in the pyridine-silver diethyldithiocarbamate. The conversion of arsenic to arsine may not be complete and this introduces a bias in the assay of the arsine tank concentration.

Test atmosphere samples at a concentration two times the OSHA standard level were generated by delivering 40.8 mg/min (818 ml/min of 15.8 ppm arsine in nitrogen, at 27.6°C and 761 mm Hg) of arsine from a gas cylinder into a dry air stream flowing at a rate of 0.1011 cu m/min. The three sample lines were maintained at dilution ratios of 0.233, 0.479 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All six samples

Table 4

Comparison of Various Collection Media for Arsine

Test concentration: 0.324 mg/cu m

Collection Media	Flowrate in Liters per Minute	% Recovery
0.01 M $AgNO_3$/0.01 M HNO_3	1.5	18
0.10 M $AgNO_3$/0.01 M HNO_3	1 - 1.5	75
0.1 M $AgNO_3$	1 - 1.5	91
3% Hydrogen peroxide	1	10
Charcoal	1	50 (Front) 18 (Backup)
Charcoal	0.2	93 (Front) 0 (Backup)

Table 5

Collection Efficiency of Arsine
(0.1 M Silver Nitrate/Impingers)
Sample Size = 110 liters

µg Found			
First Impinger	Second Impinger	Total	Collection Efficiency
35.0	3.9	38.9	0.900
33.5	3.8	37.3	0.898
33.9	3.3	37.2	0.911
34.7	3.0	37.7	0.920
34.9	2.6	37.5	0.931
33.9	3.1	37.0	0.916
		Average Collection Efficiency	0.913
		CV	0.014

Table 6

Data Sheet: Arsine, S229
Sampling and Analysis
(0.1 M Silver Nitrate/Impingers, stored for 0 days)

Test Level	Found				Taken	
	µg	Corr µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	7.80	8.57	111.3	0.0770	0.095	
	8.63	9.48	109.5	0.0866	0.095	
	9.05	9.95	109.5	0.0909	0.095	
	9.46	10.40	111.1	0.0936	0.095	
	8.53	9.37	110.4	0.0849	0.095	
	8.22	9.03	109.9	0.0822	0.095	
			n = 6			
			mean	0.0859		90.4
			std dev	0.0060		
			CV_2	0.0696		
1S	16.43	18.05	110.6	0.1632	0.201	
	18.62	20.46	111.2	0.1840	0.201	
	18.30	20.11	112.6	0.1786	0.201	
	21.22	23.32	111.5	0.2091	0.201	
	16.95	18.63	111.5	0.1671	0.201	
	18.30	20.11	110.6	0.1818	0.201	
			n = 6			
			mean	0.1806		89.9
			std dev	0.0162		
			CV_2	0.0898		
2S	36.4	40.0	109.1	0.367	0.415	
	34.8	38.2	108.8	0.351	0.415	
	35.3	38.8	110.3	0.352	0.415	
	36.1	39.7	110.8	0.358	0.415	
	36.3	39.9	110.7	0.360	0.415	
	35.2	38.7	109.5	0.353	0.415	
			n = 6			
			mean	0.357		86.0
			std dev	0.0061		
			CV_2	0.0171		
			$\overline{CV}_2$	0.0663		

Table 7

Data Sheet: Arsine, S229
Sampling and Analysis
(0.1 M Silver Nitrate/Impingers, stored for 6 days)

Test Level	Found				Taken	
	µg	Corr µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	7.86	8.64	111.4	0.0776	0.098	
	7.92	8.70	109.7	0.0793	0.098	
	7.80	8.57	109.7	0.0781	0.098	
	7.68	8.44	111.2	0.0759	0.098	
	8.69	9.55	110.6	0.0863	0.098	
	8.36	9.19	110.1	0.0835	0.098	
			n = 6			
			mean	0.0801		81.7
			std dev	0.0040		
			CV_2	0.0495		
1S	18.11	19.90	110.8	0.1796	0.204	
	18.18	19.98	111.3	0.1795	0.204	
	17.46	19.19	112.8	0.1701	0.204	
	18.75	20.60	111.6	0.1846	0.204	
	18.06	19.85	111.6	0.1779	0.204	
	16.83	18.49	110.8	0.1669	0.204	
			n = 6			
			mean	0.1764		86.5
			std dev	0.0066		
			CV_2	0.0375		
2S	28.5*	31.3*	109.3	0.286*	0.415	
	37.0	40.7	108.9	0.374	0.415	
	37.2	40.9	110.5	0.370	0.415	
	37.2	40.9	110.9	0.369	0.415	
	38.3	42.1	110.8	0.380	0.415	
	36.2	39.8	109.7	0.363	0.415	
			n = 5			
			mean	0.371		89.4
			std dev	0.0063		
			CV_2	0.0169		
			$\overline{CV}_2$	0.0382		

* These values excluded from statistical analysis.

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at the three test levels were collected simultaneously at 0.22 liters per minute for 45 minutes (10 liters). The data are summarized in Table 9. The samples were stored for 6 days before desorption and analysis.

Breakthrough

The collection efficiency on charcoal was determined based on the analysis of the front and backup sections of the charcoal tubes for sampling periods of 45-240 minutes at 0.22 liters per minute. Data are summarized in Table 8.

The first section of the charcoal tube was found to hold at least 0.022 mg of arsine when a test atmosphere containing 0.405 mg/cu m of arsine in air was sampled at 0.227 liters per minute for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_2 = 0.0253 \qquad \overline{CV}_T = 0.056$$

The average recovery of the generated samples over all levels was 93.9%.

Because the desorption efficiency was not determined as explained in the procedure section, the results should be corrected by this average recovery to reflect the undetermined desorption efficiency factor. The NIOSH Method S229 (Sampling and Analytical Method), however, was written with the usual protocol of determining desorption efficiency for the concentration range studied. The DE experiments can be done using a more concentrated arsine source, such as 15% in nitrogen. With a 15% arsine source, only 20-80 microliters of gas are needed to cover the 0.5, 1, and 2X OSHA standard and no complications are anticipated in directly injecting these small sample volumes into the charcoal tubes.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Table 8

Collection Efficiency of Arsine
Lot 105 Charcoal, 0.22 liters per minute
2S OSHA Standard: 0.405 mg/cu m

Sample Size Liters	µg Arsine Found[Δ] Front	Backup	Total	% Front
10.16	4.16	0.01	4.17	99.8
10.25	3.99	0.00	3.99	100
10.66	4.07	0.00	4.07	100
10.25	4.05	0.00	4.05	100
10.25	3.94	0.00	3.94	100
10.20	3.93	0.00	3.93	100
27.01	10.58	0.01	10.59	99.9
27.25	11.70	0.01	11.71	99.9
42.5	16.66	0.01	16.67	99.9
40.9	17.06	0.00	17.06	100.0
54.5	21.01	0.00	21.01	100.0
54.3	22.57	0.00	22.57	100.0

Overall collection efficiency 99.96%

(Δ) All values have not been corrected for desorption efficiency.

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Table 9

Data Sheet: Arsine, S229
Sampling and Analysis
(Lot 105 Charcoal, sample stored 6 days)

Test Level	Found			Taken	
	µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.865	10.16	0.0851	0.0941	
	0.832	10.25	0.0812	0.0941	
	0.857	10.20	0.0840	0.0941	
	0.859	10.43	0.0824	0.0941	
	0.859	10.02	0.0857	0.0941	
	0.809	10.16	0.0796	0.0941	
		n = 6			
		mean	0.0830		88.2
		std dev	0.00236		
		CV_2	0.0284		
1S	1.957	10.25	0.1909	0.1935	
	1.907	10.20	0.1870	0.1935	
	1.917	10.43	0.1838	0.1935	
	1.857	10.25	0.1812	0.1935	
	1.936	10.25	0.1889	0.1935	
	1.956	10.25	0.1908	0.1935	
		n = 6			
		mean	0.1871		96.7
		std dev	0.00393		
		CV_2	0.0210		
2S	4.16	10.16	0.409	0.404	
	3.99	10.25	0.389	0.404	
	4.07	10.66	0.382	0.404	
	4.05	10.25	0.395	0.404	
	3.94	10.25	0.384	0.404	
	3.93	10.20	0.385	0.404	
		n = 6			
		mean	0.391		96.8
		std dev	0.0101		
		CV_2	0.0258		
		$\overline{CV}_2$	0.0253		

Backup Data Report

Substance:	Hydrazine, No. S237
OSHA Standard:	1 ppm (1.3 mg/cu m) - skin
Chemical Used for Validation:	Hydrazine Matheson, Coleman, and Bell

Procedure

The procedure validated for collecting and measuring hydrazine in air is described in NIOSH Method S237. The analysis is based on the colorimetric method described in Reference No. 1. Standard samples were prepared and a standard curve was constructed by plotting absorbance versus μg of hydrazine. Samples of hydrazine were generated as described below and collected in midget bubblers (bubblers fitted with fritted glass tipped inlet tubes) containing 10 ml of 0.1 M hydrochloric acid. Collection efficiency was determined to be 1.00. The amounts of hydrazine found (μg) in the generated samples were determined from a standard curve. The concentration of hydrazine in air was determined by dividing the μg found by the sample volume (critical orifice flow rate for that sample x 100 minutes).

Modifications

There were no major modifications of the method described in Reference No. 1.

Analysis

The validation of the analytical method and calibration curve were conducted using a standard stock solution of hydrazine in methanol (30.3 μg/μl).

A time study indicated that the collected samples in dilute hydrochloric acid could be stored at room temperature as long as six days in a stoppered container before analysis with no loss. Six samples at 1X the OSHA level were prepared by spiking an appropriate amount of standard solution of hydrazine in methanol (30.3 μg/μl) into 10 ml of 0.1 M hydrochloric acid. The six-day results are given on the next page.

TIME STUDY OF HYDRAZINE AFTER SIX DAYS

µg added	µg found after 6 days		Recovery
121.3	122.5		1.010
121.3	125.3		1.033
121.3	122.1		1.007
121.3	124.4		1.026
121.3	123.9		1.021
121.3	119.4		0.984
		mean	1.014
		std dev	0.017

The results for immediate analysis are given at the 1S level in the table labelled Analysis.

Generation

Hydrazine was introduced into an air stream with an automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe filled with 30% solution of hydrazine in methanol (V/V) was placed in the syringe drive mechanism. The syringe, which was attached to a 15-in. long stainless steel needle, delivered the analyte at a rate of 1.97 µl/min into a heated glass tube which was heated to approximately 75°C with a heating lamp. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.6 liters/minute and diluted with air to obtain a concentration of approximately two times the OSHA standard. The actual concentration in the generator was lower than that predicted from the above data. Further dilutions with air were made to obtain two lower concentrations. The dilution system is described in Reference No. 2.

The found concentrations at 1X and 0.5X the OSHA standard level were acceptable, but the 2X level was too low. Therefore, a second generation attempt was conducted to generate six additional samples for the 2X level. The conditions for the second generation were the same as the previous generation except that the dilution air flow rate was readjusted. The concentration for the 2X level was found to be acceptable. Therefore, the 0.5X and 1X levels from the first generation and the 2X level from the second generation were used for the statistical analysis of the data. The "true" concentration at the three levels could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates possibly because of the instability of hydrazine due to oxidation and decomposition upon contact with the atmosphere (Reference No. 1). Samples were collected for 100 minutes at approximately 1.0 liter per minute.

Collection Efficiency

The collection efficiency was determined by connecting two bubblers in series at each of six sampling ports. The collection efficiency

experiments were conducted at a concentration of 3.44 mg/cu m (as determined by analysis of the front and backup bubblers). The results are given below.

HYDRAZINE COLLECTION EFFICIENCY

µg found front bubbler	µg found backup bubbler	Collection Efficiency
321	1.16	0.996
326	0.92	0.997
304	0.40	0.999
251	1.40	0.994
337	0.68	0.998
334	0.60	0.998
	mean	0.997
	std dev	0.002

The collection efficiency in a single bubbler was sufficient so it was not considered appropriate to apply a collection efficiency correction.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.031$ $\overline{CV}_2 = 0.079$ $\overline{CV}_T = 0.094$

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Data Sheet: Hydrazine S237

Analysis

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
60.7	66.6	1.097	121.3	121.6	1.002	242.6	244.4	1.007
60.7	63.0	1.038	121.3	120.7	0.995	242.6	250.7	1.033
60.7	63.5	1.046	121.3	117.6	0.970	242.6	241.6	0.996
60.7	61.6	1.015	121.3	118.0	0.973	242.6	240.3	0.991
60.7	57.1	0.941	121.3	120.3	0.992	242.6	241.6	0.996
60.7	62.1	1.023	121.3	118.0	0.973	242.6	246.2	1.015
n =		6			6			6
mean		1.027			0.984			1.006
std dev		0.051			0.014			0.016
CV_1		0.050			0.014			0.016

$\overline{CV}_1$ 0.031

$\overline{CV}_{A+\overline{AMR}}$ 0.033

Data Sheet: Hydrazine S237

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	51.6	94.5	0.546
	59.4	96.4	0.616
	58.0	97.2	0.597
	63.0	94.1	0.670
	47.5	88.9	0.534
	52.5	91.6	0.573
		n = 6	
		mean	0.589
		std dev	0.050
		CV_2	0.085
1S	133.0	95.2	1.397
	124.4	90.9	1.368
	132.6	90.2	1.470
	139.8	89.2	1.567
	105.3	84.5	1.246
	118.0	87.0	1.356
		n = 6	
		mean	1.401
		std dev	0.109
		CV_2	0.078
2S	321	91.6	3.50
	326	96.0	3.40
	304	87.6	3.47
	251	84.5	2.97
	337	92.0	3.66
	334	92.3	3.62
		n = 6	
		mean	3.44
		std dev	0.25
$\overline{CV}_2$ 0.079		CV_2	0.073

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

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References

1. Dambrauskas, Thomas and Cornish, Herbert, "A Modified Spectrophotometric Method for the Determination of Hydrazine," Industrial Hygiene Journal, 23 (1962) 151.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Hydrogen Chloride, No. S246

OSHA Standard: 5 ppm (7 mg/cu m) - Ceiling

Chemical Used for Validation: Hydrogen Chloride in Nitrogen - 1000 ppm HCl
Matheson Gas Products

Procedure

The procedure for validation of the method for collecting and measuring concentrations of hydrogen chloride in air is described in NIOSH Method S246, which has been adapted from P&CAM 115. The reliability of the analytical method was tested at sample concentrations equal to that present in a 15-minute sample at 0.5, 1, and 2 times the OSHA standard level, when sampled at 1.0 liter per minute. The appropriate aliquot (0.15, 0.30, and 0.60 ml) of a 0.352 mg/ml solution of chloride ion in 0.5 M sodium acetate was added to 10 ml of 0.5 M sodium acetate and a dilution to 25 ml was made with distilled water. The analyses were performed using an Orion Model 94-17A chloride specific ion electrode, reference electrode Orion 90-02 double junction, and an Orion Model 407 specific ion meter (using millivolt and expanded millivolt scales). Details of the analytical procedures may be found in Section 8.4 of NIOSH Method S246.

Test atmospheres of hydrogen chloride at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected in midget bubblers containing 10 ml of 0.5 M sodium acetate. The results of the analyses of these samples are given in the sampling and analysis table.

Modification

There was one major modification made to P&CAM 115. It is necessary to use polyethylene containers to ship the collected samples, because a time study on spiked samples showed a loss of hydrogen chloride over a period of five days. (See Discussion Section)

Generation

The concentration of hydrogen chloride in the cylinder was checked by allowing a flow rate of 0.472 liter per minute of the mixture to bubble through three midget bubblers in parallel (fitted with Teflon gas delivery tubes) containing 75% acetic acid for 2 minutes 7 seconds. The solution in each of the bubblers was analyzed by potentiometric titration with 0.01 M silver nitrate using a chloride ion specific electrode. From the amount of chloride ion found, and the flow rate of hydrogen chloride out of the cylinder, the concentration of hydrogen chloride in the cylinder was calculated. The average concentration was determined to be 1034 mg/cu m or 713 ppm hydrogen chloride.

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At 2X the OSHA standard level, a flow rate out of the hydrogen chloride cylinder was set at 472 ml/minute. This flow was diluted with 34.4 liters/minute of air to give a "taken" concentration of 14.00 mg/cu m. At 1X the OSHA standard level, the flow out of the cylinder was 244 ml/minute, and the dilution air was 35.6 liters/minute. This gave a "taken" concentration of 7.00 mg/cu m. At 0.5X the OSHA standard level, a cylinder flow rate of 105 ml/minute and dilution air of 30.8 liters/minute gave a taken concentration of 3.50 mg/cu m.

The generation apparatus was made entirely of Teflon. A schematic drawing is presented in Figure 1.

Six sampling ports are arranged on opposite sides of the tube at intervals of 7, 8, 9, 10, 11, and 12 inches from end A. The apparatus is placed in a hood such that the hydrogen chloride vapor exhaust does not pose a contamination hazard. Hydrogen chloride is introduced into the apparatus from the cylinder via a 1/4-in. O.D. Teflon tube. The entire system was passivated for approximately one day with the hydrogen chloride-nitrogen mixture from the cylinder. Six samples at each of the three levels were collected in midget bubblers containing 10 ml of 0.5 M sodium acetate. Samples were collected for 15 minutes at a rate of approximately 1.0 liter/minute (individual critical orifices give slightly different flow rates).

Collection Efficiency

A collection efficiency experiment was performed at 70 mg/cu m to determine the amount of hydrogen chloride that would pass through a single midget bubbler at a flow rate of approximately 0.94 liter/minute for a 15-minute sampling period. The experiment was performed by placing a second midget bubbler downstream of the primary bubbler. Thus, any hydrogen chloride vapor not collected in the first bubbler would be trapped in the second bubbler. The results are given in the following table:

COLLECTION EFFICIENCY OF HYDROGEN CHLORIDE

µg found front bubbler	µg found backup bubbler	Collection Efficiency
1016	19.6	0.981
955	19.4	0.980
941	19.3	0.980
1000	18.9	0.981
1016	19.6	0.981
1000	19.0	0.981
	mean	0.981
	std dev	0.001

Since collection efficiency for hydrogen chloride was determined to be 0.981, no recovery correction is necessary.

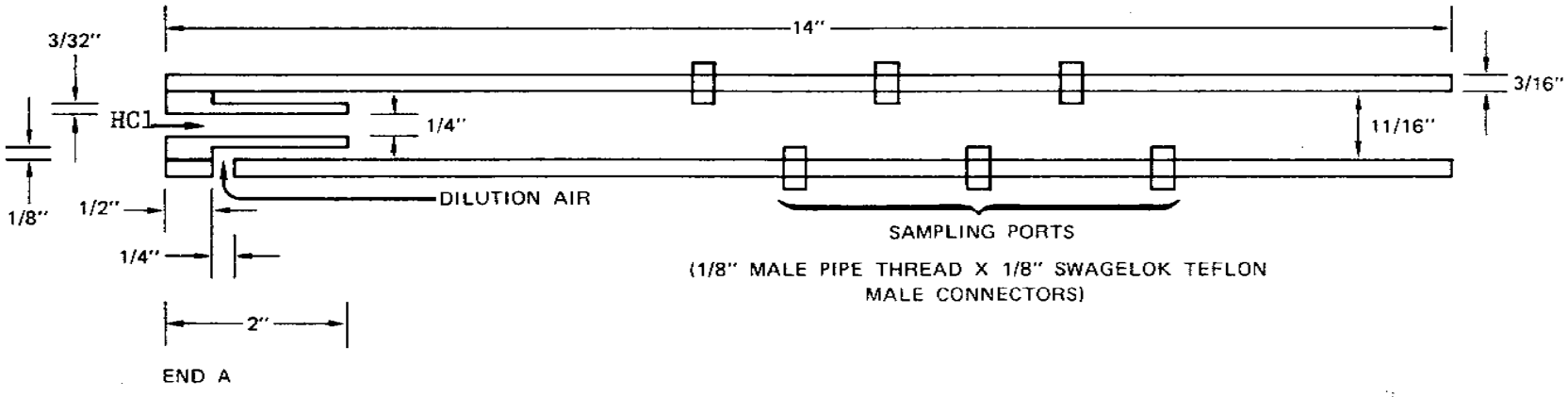

FIGURE 1 CROSS SECTION OF THE GENERATION APPARATUS FOR HYDROGEN CHLORIDE

Discussion

A time study was conducted at the 1X level by spiking 0.30 ml of a 0.352 mg/ml solution of chloride ion in sodium acetate to 10 ml of 0.5 M sodium acetate contained in a midget bubbler. The samples were allowed to stand for five days before analysis.

For analysis, the solutions in the bubblers were quantitatively transferred to pre-marked beakers. The beakers were pre-marked at 25 ml. The bubblers were rinsed three times with distilled water and the rinses were added to the beaker. A final dilution to 25 ml was made with distilled water. The solutions were analyzed with an Orion Model 94-17A chloride specific ion electrode, reference electrode Orion 90-02 double junction, and an Orion Model 407 specific ion meter. The results of the time study are given below:

µg taken	µg found		Recovery
106	92		0.868
106	92		0.868
106	91		0.858
106	94		0.887
106	94		0.887
106	90		0.849
		mean	0.870
		std dev	0.015

These recoveries were compared with the 1X recoveries in the Analysis table which represents samples that were analyzed immediately. Because of the low recoveries using glass bubblers to store samples, it was decided to test the use of polyethylene containers. The time study was repeated using polyethylene containers. The results of the second time study are given below:

µg taken	µg found		Recovery
106	105		0.991
106	105		0.991
106	101		0.953
106	104		0.981
106	104		0.981
106	102		0.962
		mean	0.976
		std dev	0.016

The above results support the conclusion that hydrogen chloride should be shipped and stored in polyethylene containers.

Precision and Accuracy

The statistical procedures used are described in Reference No. 1.

$\overline{CV}_1 = 0.019$ $\overline{CV}_2 = 0.039$ $\overline{CV}_T = 0.064$

The average recovery at the OSHA standard level was 102.7%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Hydrogen Chloride S246

Analysis

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
53	54	1.019	106	110	1.038	213	212	0.995
53	53	1.000	106	110	1.038	213	218	1.023
53	55	1.038	106	107	1.009	213	211	0.991
53	54	1.019	106	108	1.019	213	219	1.028
53	54	1.019	106	106	1.000	213	215	1.009
53	52	0.981	106	104	0.981	213	217	1.019
n =		6			6			6
mean		1.013			1.014			1.011
std dev		0.020			0.022			0.015
CV_1		0.020			0.022			0.015

$\overline{CV}_1$ 0.019

$\overline{CV}_{A+\overline{AMR}}$ 0.021

The average A.M.R. at each level is so close to 1.0 that no A.M.R. correction is needed.

Data Sheet: Hydrogen Chloride S246

Sampling and Analysis

Test Level	Found			Taken	
	µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	54	13.84	3.90	3.50	
	55	14.07	3.91	3.50	
	52	14.76	3.52	3.50	
	49	14.52	3.37	3.50	
	54	14.52	3.72	3.50	
	56	15.00	3.73	3.50	
		n = 6			
		mean	3.69		105.4
		std dev	0.21		
		CV_2	0.057		
1S	104	14.07	7.39	7.00	
	102	13.84	7.37	7.00	
	108	15.00	7.20	7.00	
	101	14.52	6.96	7.00	
	105	14.52	7.23	7.00	
	103	14.76	6.98	7.00	
		n = 6			
		mean	7.19		102.7
		std dev	0.18		
		CV_2	0.025		
2S	202	15.00	13.47	14.00	
	192	13.84	13.87	14.00	
	193	14.07	13.72	14.00	
	148	14.76	10.03*	14.00	
	192	14.52	13.22	14.00	
	202	14.52	13.91	14.00	
		n = 5			
		mean	13.64		97.4
		std dev	0.29		
$\overline{CV}_2$ 0.039		CV_2	0.021		

* This value did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Carbon Disulfide, No. S248

OSHA Standard: Ceiling - 30 ppm
Peak - 100 ppm
T.W.A. - 20 ppm

Chemical Used for Validation: Carbon Disulfide
Mallinckrodt

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of carbon disulfide in air is described in NIOSH Method S248, which has been adapted from the method described in Reference No. 1. Desorption efficiency tests were done at 2X, 1X, and 0.5X the OSHA ceiling standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of carbon disulfide to represent 6-liter air samples. Samples of carbon disulfide in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. Each charcoal tube was preceded with a sodium sulfate drying tube to prevent moisture from entering the charcoal tube during sampling. The temperature and pressure were 22°C and 766 mm Hg. The samples were desorbed with benzene and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of carbon disulfide in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample times 10 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA ceiling standard levels were determined from the delivery rate of a calibrated automated Harvard infusion/withdrawal pump and the flow rates of the dilution air. The total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modification

A benzene solution of carbon disulfide containing 0.14 mg/microliter was used to apply the analyte onto the charcoal. This was done so it would not be necessary to inject less than two microliters at the 0.5X level.

Generation

Samples of carbon disulfide in air were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950) and a three-stage dilution system. A 2-ml syringe was filled with carbon disulfide and placed in the syringe drive pump. The syringe, which was attached to a 15-inch long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 6.55 mg per minute. The tube was packed with glass wool to provde a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.09 liters per minute and diluted with air at a rate of 28.0 liters per minute to obtain the 2X concentration level. Further dilution with air was made to obtain concentrations that were 1X and 0.5X the OSHA standard. The dilution system is described in Reference No. 2. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

The concentration in the three sampling chambers were determined from the delivery rate of the syringe drive and the flow rates of the dilution air.

Samples were collected for 30 minutes at an average flow rate of 0.20 liter per minute.

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as follows. A calibrated automated Harvard infusion/withdrawal pump was used to deliver the analyte, and the same conditions that were used during generation of test atmospheres were also used for the breakthrough test. For the breakthrough test, the backup sections of the charcoal tubes were removed. The sodium sulfate drying tubes were connected in series to the front of the charcoal tubes. Connected to the back of the charcoal tubes were midget bubblers containing 15 ml of Viles reagent (Reference No. 3). The Viles reagent is able to detect less than 1 ng of carbon disulfide, therefore, the Viles reagent was used for the breakthrough test. Visual standards were prepared at a concentration of 94 mg/cu m (5% of the 2X level). Breakthrough occurred at 162 minutes when the color in the bubbler matched the color of the standard.

Discussion

It was necessary to prepare drying tubes to precede the charcoal tube during sampling. Experiments conducted by NIOSH (Reference No. 1) showed that there was increasing loss of carbon disulfide with an increase in relative humidity. It was determined that 270 mg of anhydrous sodium sulfate in the drying tube would be sufficient to remove any moisture in the air. This amount was determined by assuming a 6-liter sample collected at 22°C with 100% relative humidity.

A time study was conducted. One hundred-milligram portions of 20/40 mesh charcoal Lot 105 were spiked at 1X the ceiling OSHA standard. Four microliters of a benzene solution of carbon disulfide was used to spike the charcoal (0.14 mg/microliter). The samples were allowed to stand for one week before analysis. The samples were desorbed with 10 ml of benzene and a 5-microliter aliquot was analyzed by GC. The results of the time study were compared with the D.E. results in the Analysis table, which represents samples which were analyzed immediately. The results of the time study are given below. From these results, it was concluded that carbon disulfide is stable on charcoal for at least one week.

TIME STUDY RESULTS FOR CS_2

mg taken	mg found		Recovery
0.560	0.480		0.857
0.560	0.450		0.804
0.560	0.460		0.821
0.560	0.490		0.875
0.560	0.500		0.893
0.560	0.490		0.875
		mean	0.854
		std dev	0.035
		CV	0.041

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.052$ $\overline{CV}_2 = 0.022$ $\overline{CV}_T = 0.059$

The average recovery at the ceiling OSHA standard level was 99.3%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

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Data Sheet: Carbon Disulfide S248

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
0.280	0.214	0.764	0.560	0.414	0.739	1.120	1.160	1.036
0.280	0.212	0.757	0.560	0.450	0.804	1.120	1.100	0.982
0.280	0.208	0.743	0.560	0.472	0.843	1.120	1.200	1.071
0.280	0.208	0.743	0.560	0.460	0.821	1.120	1.160	1.036
0.280	0.204	0.729	0.560	0.520	0.929	1.120	1.120	1.000
0.280	0.216	0.771	0.560	0.430	0.768	1.120	1.120	1.000
n =		6			6			6
mean		0.751			0.817			1.021
std dev		0.016			0.066			0.033
CV_1		0.021			0.081			0.032

$\overline{CV_1}$ 0.052

$\overline{CV_{A+\overline{DE}}}$ 0.056

A hand drawn curve using the above data was used to determine the corr. mg in the Sampling and Analysis table.

Data Sheet: Carbon Disulfide S248

Sampling and Analysis

Test Level	Found					Taken	
	mg	Corr mg	Liters	mg/cu m	ppm*	ppm	Recovery (%
0.5S	0.192	0.259	5.86	44.2	13.92	14.71	
	0.204	0.272	6.03	45.1	14.21	14.71	
	0.220	0.293	6.19	47.3	14.90	14.71	
	0.196	0.261	5.75	45.4	14.33	14.71	
	0.196	0.261	5.79	45.1	14.21	14.71	
	0.192	0.259	5.62	46.1	14.52	14.71	
				n = 6			
				mean	14.35		97.6
				std dev	0.33		
				CV_2	0.023		
1S	0.400	0.500	5.26	95.1	30.0	29.4	
	0.396	0.495	5.22	94.8	29.9	29.4	
	0.340	0.430	4.70	91.5	28.8	29.4	
	0.370	0.462	5.09	90.8	28.6	29.4	
	0.380	0.475	5.20	91.3	28.8	29.4	
	0.400	0.500	5.38	92.9	29.3	29.4	
				n = 6			
				mean	29.2		99.3
				std dev	0.6		
				CV_2	0.021		
2S	1.080	1.080	6.00	180.0	56.7	58.8	
	1.100	1.100	5.86	187.7	59.1	58.8	
	1.060	1.060	5.56	190.6	60.0	58.8	
	1.060	1.060	5.56	190.6	60.0	58.8	
	1.000	1.000	5.26	190.1	59.9	58.8	
	1.050	1.050	5.56	188.8	59.5	58.8	
				n = 6			
				mean	59.2		100.7
				std dev	1.3		
$\overline{CV}_2$ 0.022				CV_2	0.022		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. McCammon C., Quinn, P., and Kupel R., "A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide," Amer. Ind. Hyg. Assoc. J., 36, 618, August 1975.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Viles, F. J., "Field Determinations of Carbon Disulfide in Air," J. Of Ind. Hyg. and Tox., 22, 188, (1940).

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Cyanide (as CN), No. S250

OSHA Standard: 5 mg/cu m

Chemical Used for Validation: Potassium Cyanide, Fisher Scientific Co., 98%

Procedure

The general procedure recommended is described in NIOSH Method No. S250 which has been adapted from P&CAM 116, cyanide by ion specific electrode. The cyanide samples are collected on a filter and 0.1N NaOH/impinger "train" in order to collect the particulate cyanide as well as any HCN present or formed. Tests indicate that during the collection of particulate cyanide, interaction with atmospheric moisture can cause some decomposition to HCN, and therefore the filter must be backed up with the caustic-containing impinger. The method cannot distinguish between the HCN present in the environment as such and the HCN formed from the collected particulate cyanide during the sampling period.

The samples were analyzed using an ion specific electrode for cyanide, Orion Model 94-06, and a digital pH meter, Orion Model 801. An Orion Model 90-20-00 double junction, silver-silver chloride electrode was used as reference. Details of the analytical procedure may be found in Section 8.3 of NIOSH Method No. S250.

An estimate of the reliability of the analytical method was obtained by analyzing only a set of six filters loaded with 1.830-2.555 mg of KCN (0.732-1.022 mg CN). For this set of samples good recovery and precision were obtained, 97% with $CV_1 = 0.038$. These analytical samples were prepared by adding individually-weighed amounts of KCN to each filter. The sample size studied is equivalent to that present in a 90-liter sample at 2X the OSHA standard for cyanide. No attempt was made to prepare the equivalent analytical sets for the 0.5 and 1X OSHA standard test level because of the low precision associated with weighing less than 1 mg of material. We found that spiking by using aqueous or basic solutions of potassium cyanide proved to be unsuccessful because of the cyanide instability in the presence of water and CO_2. The data showing poor recoveries when cyanide solutions were used for spiking are shown in Table 1B.

Modification

P&CAM 116 was modified by recommending the use of a filter before the 0.1N NaOH/impinger. The standard for particulate cyanide is different from that of HCN, 5 mg/cu m vs. 11 mg/cu m respectively, and the method is presented to be able to give a cursory distinction between the two species. Note, however, that the HCN found may be due to "free" HCN plus the HCN that could be formed from the collected particulate cyanide during the sampling period.

TABLE 1

Analytical Recovery of Cyanide as CN from Filters

A. Spiked with solid KCN (filters stored overnight).

µg added	µg Found	Recovery
732	108*	0.148*
854	803	0.940
897	904	1.008
892	908	1.018
853	813	0.953
1022	966	0.945
	n = 5	
	mean	0.973
	std dev	0.0372
	CV_1	0.0382

B. Spiked with solutions of KCN.

Spiking Solution	Filter Storage Time	µg added	µg found	Recovery
KCN in Water	1 hour	900	853	0.948
KCN in Water	1 day	900	83	0.092
KCN in Water	1 day	450	76	0.169
KCN in Water	1 day	225	25	0.111
KCN in 0.1N NaOH	1 day	900	140	0.155
	1 day	900	163	0.181
	1 day	900	151	0.168
	1 day	900	212	0.235
	1 day	900	130	0.144
	1 day	900	130	0.144

*Value excluded from calculation based on Grubb's Test.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of potassium cyanide containing 64.9 g/liter as cyanide into a dry, solvent-free air stream flow. The atomizer flow rate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 60 minutes (90 liters). Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate cyanide was determined by sampling air sample concentrations equivalent to 2X OSHA standard. A set of six samples were collected on front and backup filters arranged in the three-piece cassette holder such that the front filter is set on the grooves of the holder and is physically separated from the backup filter which is supported by the backup pad. Each filter was analyzed separately and on the basis of the amount of cyanide found in the front and the backup filters, the collection efficiency of particulate cyanide was found to be 100.0% (Table 2).

Discussion

The cyanide salts are known to decompose in moist air with liberation of hydrogen cyanide; the data in Table 1B demonstrate this instability. Thus, further experimental tests were conducted in order to determine the extent of conversion of particulate cyanide to HCN.

Two separate sets of 6 samples, representative of a 90-liter sample at each of the 1 and 2X OSHA standard test levels were used for these studies (Table 3). In each case, the experimental study was conducted such that after collecting 90 liters of air samples containing controlled amounts of particulate cyanide, an additional 90 liters of air free of particulate cyanide was drawn through each of 3 samples while the other 3 samples served as controls. Note that for the samples at 2X OSHA standard (Table 3B), the sampling train consisted of a filter connected in series to two impingers each containing 10 ml of 0.1 N NaOH; particulate cyanide is collected on the filter while HCN is collected in the 0.1 N NaOH/impingers. Note that solutions of cyanide in 0.1N NaOH were found to be stable for at least 5 days.

The data summarized in Table 3 show a consistent loss of CN from the filters after air is drawn. Under the experimental conditions employed for these studies, the relative amount of cyanide lost from

TABLE 2

Collection Efficiency: Cyanide (as CN), S250

µg Found			% Collected
Front	Backup	Total	in Front
749	ND	749	100
782	ND	782	100
570	ND	570	100
815	ND	815	100
783	ND	783	100
682	ND	682	100

Average Collection Efficiency..... 100

ND = No Detectable Cyanide; the lower limit of detection is 3 µg/25 ml.

TABLE 3

Decomposition of Particulate CN to HCN

A. Equivalent to 90-liter sample at OSHA standard.

Sample Code	Test Condition[1]	µg Found on Filter[2]
7	Additional Air	312
8	Additional Air	333
9	Additional Air	283
	Average	309
10	No Additional Air	360
11	No Additional Air	380
12	No Additional Air	371
	Average	370
	Cyanide loss for filter =	16.5%

B. Equivalent to 90-liter sample at 2X OSHA standard.

Sample Code	Test Condition[1]	µg Found		
		Filter	Front Impinger	Backup Impinger
13	Additional Air	617	681	20.4
14	Additional Air	573	923	15.2
15	Additional Air	573	982	21.8
	Average	588	862	19.1
16	No Additional Air	697	587	6.3
17	No Additional Air	711	540	3.5
18	No Additional Air	705	557	5.9
	Average	704	561	5.2

Cyanide loss from filter = 16.5%

1. Defines whether or not an additional 90 liters of air (free of particulate cyanide) was drawn through the sampling train.
2. The filter was not backed up with any other sampling media.

the filter is 16.5%. This loss is expected to be strongly dependent on such factors as--humidity, particle size and total surface area--therefore the value cannot be recommended as a general correction factor to determine total particulate cyanide. Table 3B also indicates that a large amount of HCN is found in the backup impingers. This high HCN value is believed to be an artifact in the process of generating the particulate cyanide test atmosphere since an aqueous solution of KCN was atomized into the generation/dilution system. Note also that a higher amount of HCN is found in the impinger for samples 13-15 relative to what would be reasonable to expect based on the average amount lost from the filters. This observation is probably due to the fact that the additional air drawn through the filters was taken from the dilution system which had cyanide on the walls and would therefore generate extra HCN.

All the data obtained indicate that for the collection of particulate cyanide, a front filter in series with 0.1N NaOH/impinger should be used. The collection efficiency of dry particulate cyanide has been shown to be 100% (Table 2) and the collection efficiency for HCN in 0.1N NaOH was at least 98% based on the relative amounts found in the front and backup impingers of six samples (Table 3B).

Precision and Accuracy

The statistical procedures used are described in Reference 1. The data for the set of 18 collected samples are shown in Table 4.

$\overline{CV}_2 = 0.0901$ $\overline{CV}_T = 0.103$

In view of the observed decompositional losses of particulate CN from the filter during the sample collection period, the uncorrected mg/cu m found cannot be taken as a measure of generator concentration. A better estimate of the generator concentration for this validation study can be obtained by correcting for the amount of particulate CN which decomposed to HCN. This conversion has been estimated to be 16.5% only for these specific experimental studies. Thus, the generator concentration for this validation study is estimated to be 2.62, 5.60, and 9.68 mg/cu m respectively for the 0.5, 1 and 2X OSHA standard test levels.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 4

Data Sheet: Cyanide as CN, S250

Sampling and Analysis
(Samples Collected on Cellulose Membrane Filter)

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	205.1	91.7	2.237
	221.8	91.8	2.416
	192.8	91.3	2.112
	196.3	92.0	2.134
	38.1*	92.5	0.412*
	187.9	91.9	2.045
		n = 5	
		mean	2.189
		std dev	0.1425
		CV_2	0.0650
1S	407	91.7	4.44
	419	91.6	4.57
	429	91.6	4.68
	447	91.6	4.88
	467	91.4	5.11
	407	92.3	4.41
		n = 6	
		mean	4.68
		std dev	0.2711
		CV_2	0.0579
2S	749	90.3	8.29
	782	90.2	8.67
	570	90.3	6.31
	815	90.2	9.04
	783	90.0	8.70
	682	91.0	7.49
		n = 6	
		mean	8.08
		std dev	1.018
		CV_2	0.1260
		$\overline{CV}_2$	0.0901

*Value excluded from calculation based on Grubb's Test.

Backup Data Report

Substance: Dimethyl Acetamide, No. S254

OSHA Standard: 10 ppm (35 mg/cu m) - skin

Chemical Used for Validation: Dimethyl Acetamide
Aldrich

Procedure

The procedure for collecting dimethyl acetamide in air and measuring its concentration is described in NIOSH Method S254, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of dimethyl acetamide to represent 50-liter air samples. Samples of dimethyl acetamide in air were generated by a syringe drive system and a 3-stage dilution system. Samples were collected in silica gel tubes. The analyte was desorbed with methanol and its concentration was measured by gas chromatography using an automatic sample injector. The amounts measured were corrected for desorption efficiency (D.E.) to determine corrected mg. The "found" concentration in air was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 52 minutes). It was found that the "true" concentrations at the 2X, 1X, and 0.5X OSHA standard level could not be determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. Some dimethyl acetamide was apparently lost in the system. Therefore, collection efficiency was determined by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00 at a detection limit of 0.9 mg/cu m. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were four major modifications to P&CAM 127.

1. The analyte was collected on 20/40 mesh silica gel instead of 20/40 mesh activated charcoal. The silica gel tubes were 7-cm long by 4-mm I.D. and contained approximately 150 mg of silica gel in the adsorbing section and 75 mg in the backup section.

*Silica gel tubes manufactured by Bal-Labs, Santa Clara, California were used in this study.

2. A solution of dimethyl acetamide in acetone, containing 472 μg/μl was used to apply the analyte to the silica gel for desorption efficiency determinations. A solution was used so it would not be necessary to inject less than 2 μl at the 0.5X level.

3. Methanol was used as the eluent instead of carbon disulfide.

4. An ultrasonic bath was used to aid desorption.

Generation

Samples of dimethyl acetamide in air were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950) and a 3-stage dilution system. A 2-ml syringe was filled with dimethyl acetamide and placed in the syringe drive pump. The syringe, which was attached to a 15-in. long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 7.45 mg/minute. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 6.95 liters/minute and diluted with air at a rate of 62.5 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain concentrations that were 1X and 0.5X the OSHA standard. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

The concentration of the generated samples at each level was found to be lower than expected. It is assumed that the cause of the low values was loss of the analyte in the generator. This being the case, the "true" concentrations at the 2X, 1X, and 0.5X the OSHA standard level could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates. Collection efficiency was determined to be 1.00. Therefore, the "found" and "true" concentrations were considered to be equal.

Samples were collected for 52 minutes at a rate of approximately 0.88 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2 using the syringe drive pump. A syringe drive pump was used to generate the analyte at a concentration of 105.6 mg/cu m (as determined by analyses of samples taken at the 2X level). A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 105.6 mg/cu m was present in the effluent after 240 minutes of sampling at a rate of approximately 0.876 liter/minute, at which time the test was discontinued. Breakthrough was not observed.

Collection Efficiency

Collection efficiency tests were conducted at a concentration of 105.6 mg/cu m by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00, since no dimethyl acetamide was detected at a detection limit of 0.89 mg/cu m. The results of the collection efficiency test are presented below:

mg/cu m found front section	mg/cu m found backup section	Collection Efficiency
104.2	N.D.	1.00
109.1	N.D.	1.00
105.9	N.D.	1.00
104.5	N.D.	1.00
106.6	N.D.	1.00
103.0	N.D.	1.00

Discussion

Preliminary desorption efficiency tests on dimethyl acetamide were not conducted on charcoal, because the desorption efficiency of dimethyl formamide was poor (Reference No. 3) and it was assumed that desorption efficiency on charcoal would not be satisfactory for dimethyl acetamide. Therefore, dimethyl acetamide was collected on 20/40 mesh silica gel and desorbed with 1 ml of methanol using an ultrasonic bath.

A time study was conducted by spiking 150-mg portions of 20/40 mesh silica gel at 1X the OSHA standard. Four microliters of a stock solution containing dimethyl acetamide in acetone (472 $\mu g/\mu l$) was used for spiking. The samples were allowed to stand for five days before analysis. The samples were desorbed with 1 ml of methanol in an ultrasonic bath. The results of the time study are given below:

TIME STUDY RESULTS OF DIMETHYL ACETAMIDE

mg taken	mg found		D.E.
1.886	1.768		0.937
1.886	1.761		0.934
1.886	1.748		0.927
1.886	1.769		0.938
1.886	1.795		0.952
1.886	1.748		0.927
		Mean	0.936
		Std dev	0.009

The time study results were compared with the 1X D.E.'s in the Analysis Table at the end of this report. The data in the Analysis Table represent samples which were analyzed immediately. Based on these results, dimethyl acetamide is stable on silica gel for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.032$ $\overline{CV}_2 = 0.043$ $\overline{CV}_T = 0.067$

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Data Sheet: Dimethyl Acetamide S254

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.943	0.814	0.863	1.886	1.712	0.908	3.77	3.54	0.939
0.943	0.842	0.893	1.886	1.694	0.898	3.77	3.56	0.944
0.943	0.782	0.829	1.886	1.794	0.951	3.77	3.51	0.931
0.943	0.870	0.923	1.886	1.801	0.955	3.77	3.58	0.950
0.943	0.882	0.935	1.886	1.803	0.956	3.77	3.63	0.963
0.943	0.834	0.884	1.886	1.805	0.957	3.77	3.64	0.966
n =		6			6			6
mean		0.888			0.938			0.949
std dev		0.039			0.027			0.014
CV_1		0.044			0.029			0.015

$\overline{CV}_1$ 0.032

$\overline{CV}_{A+\overline{DE}}$ 0.035

The equation D.E. = $0.946 - e^{-3.35 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 5.

Data Sheet: Dimethyl Acetamide S254

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.614	0.751	40.5	18.54
	0.650	0.780	42.8	18.22
	0.649	0.780	44.0	17.73
	0.704	0.827	46.6	17.75
	0.663	0.791	43.3	18.27
	0.702	0.825	44.6	18.50
			n = 6	
			mean	18.17
			std dev	0.35
			CV_2	0.019
1S	1.912	2.025	47.3	42.8
	1.770	1.877	45.9	40.9
	1.723	1.827	44.0	41.5
	1.830	1.939	45.9	42.2
	1.362	1.455	40.5	35.9
	1.847	1.957	44.6	43.9
			n = 6	
			mean	41.2
			std dev	2.8
			CV_2	0.068
2S	4.47	4.73	45.4	104.2
	4.55	4.81	44.1	109.1
	4.24	4.48	42.3	105.9
	4.36	4.61	44.1	104.5
	4.45	4.70	44.1	106.6
	4.17	4.41	42.8	103.0
			n = 6	
			mean	105.6
			std dev	2.2
$\overline{CV}_2$ 0.043			CV_2	0.021

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Dimethyl Formamide, No. S255, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387 (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Dimethyl Formamide, No. S255

OSHA Standard: 10 ppm (30 mg/cu m) - skin

Chemical Used for Validation: Dimethyl Formamide
J. T. Baker

Procedure

The procedure for collecting dimethyl formamide in air and measuring its concentration is described in NIOSH Method S255, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of dimethyl formamide to represent 50-liter air samples. Samples of dimethyl formamide were generated by a syringe drive system and a 3-stage dilution system. Samples were collected in silica gel tubes. The analyte was desorbed with methanol and its concentration was measured by gas chromatography using an automatic sample injector. The amounts measured were corrected for desorption efficiency (D.E.) to determine corrected mg. The "found" concentration in air was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 52.5 minutes). It was found that the "true" concentrations at 2X, 1X, and 0.5X the OSHA standard level could not be determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. Therefore, collection efficiency was determined by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00 at a detection limit of 0.7 mg/cu m. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were four major modifications to P&CAM 127.

1. The analyte was collected on 20/40 mesh silica gel instead of 20/40 mesh activated charcoal. The silica gel tubes were 7-cm long by 4-mm I.D. and contained approximately 150 mg of silica gel in the adsorbing section and 75 mg in the backup section.

2. A solution of dimethyl formamide in acetone, containing 380 μg/μl, was used to apply the analyte to the silica gel for desorption efficiency determinations. A solution was used so it would not be necessary to inject less than approximately 2 μl at the 0.5X level.

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*Silica gel tubes were obtained from Bal-Labs, Santa Clara, California. These tubes were manufactured at Bal-Labs.

3. Methanol was used as the eluent instead of carbon disulfide.

4. An ultrasonic bath was used to aid desorption.

Generation

Samples of dimethyl formamide in air were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950) and a 3-stage dilution system. A 2-ml syringe was filled with dimethyl formamide and placed in the syringe drive pump. The syringe, which was attached to a 15-in long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 7.44 mg/minute. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.0 liters/minute and diluted with air at a rate of 40.6 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain concentrations that were 1X and 0.5X the OSHA standard. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

The concentration of the generated samples at each level was found to be lower than expected. It is assumed that the cause of the low values was a loss of the analyte in the generator. This being the case, the "true" concentrations at the 2X, 1X, and 0.5X the OSHA standard level could not be determined from the delivery rate of the syringe drive pump and the dilution air flow rates. Collection efficiency was determined to be 1.00 based on the analysis of backup sections of silica gel tubes. Therefore, the "found" and "true" concentrations were considered to be equal.

Samples were collected for 52.5 minutes at a rate of approximately 0.86 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2 using the syringe drive pump and the dilution system. A syringe drive pump was used to generate the analyte at a concentration of 119.5 mg/cu m (as determined by analyses of samples taken). A total hydrocarbon analyzer was used to monitor the pump effluent. Breakthrough was observed when 5% of the generated concentration of 119.5 mg/cu m was present in the effluent after 146 minutes of sampling at a rate of approximately 0.86 liter/minute, at which time the test was discontinued. The breakthrough test was conducted at a concentration equivalent to 4X the OSHA standard. From these data it was concluded that dimethyl formamide will not have breakthrough in four hours if sampling is done at a concentration of 2X the OSHA standard.

Collection Efficiency

Collection efficiency tests were conducted at a concentration of 61.1 mg/cu m by analyzing the backup sections of the silica gel tubes. Collection efficiency was determined to be 1.00, since no dimethyl formamide was detected at a detection limit of 0.7 mg/cu m. The results are presented below:

mg/cu m found front section	mg/cu m found backup section	Collection Efficiency
61.3	N.D.	1.00
59.8	N.D.	1.00
59.2	N.D.	1.00
62.0	N.D.	1.00
63.1	N.D.	1.00

Discussion

Preliminary desorption efficiency tests were conducted on charcoal Lot 105 and Lot 104 at the 1X OSHA standard level for a 20-liter sample. Four microliters of a stock solution containing dimethyl formamide in acetone (0.142 mg/μl) was used to spike 100 mg of both lots of charcoal. Carbon disulfide and water were tested as possible desorbing solvents. The samples were treated for 30 minutes in 1 ml of desorbing solvent, and analyzed by gas chromatography. The GC conditions used were: 6-ft long X 1/4-in. O.D. stainless steel column packed with 20% UCON 50LB 550X on Chromosorb P 60/80 treated with 20% KOH; column temperature of 125°C; detector temperature of 240°C; injector temperature of 185°C. The results are given below:

Solid Sorbent	Desorbing Solvent (1 ml)	Recovery (%)
Charcoal Lot 104	Carbon Disulfide	0
Charcoal Lot 104	Water	8.5
Charcoal Lot 105	Carbon Disulfide	0
Charcoal Lot 105	Water	2.6

Since the recoveries of dimethyl formamide from charcoal using carbon disulfide and water were poor, desorption efficiency tests were conducted using methanol as a possible desorbing solvent. Desorption efficiency tests were conducted on charcoal Lot 104, charcoal Lot 105, and silica gel. The results are given below:

Solid Sorbent	Desorbing Solvent (1 ml)	Recovery (%)
Charcoal Lot 104	Methanol	83.9
Charcoal Lot 105	Methanol	68.7
Silica gel	Methanol	85.2

From the above results silica gel was chosen as the solid sorbent and methanol as the desorbing solvent. It was decided that further experiments on dimethyl formamide would be based on a 50-liter sample in order to increase the recovery of the analyte from the silica gel.

For the validation studies, the GC conditions were adjusted to decrease the retention time of the analyte. The conditions given in the Sampling and Analytical Method were found to be satisfactory.

A time study was conducted by spiking 150-mg portions of 20/40 mesh silica gel at 1X the OSHA standard. Four microliters of a stock solution containing dimethyl formamide in acetone (379.5 $\mu g/\mu l$) was used for spiking. The samples were allowed to stand for five days before analysis. The samples were desorbed with 1 ml of methanol in an ultrasonic bath. The results of the time study are given below.

TIME STUDY RESULTS OF DIMETHYL FORMAMIDE

mg taken	mg found		D.E.
1.518	1.393		0.918
1.518	1.399		0.922
1.518	1.385		0.912
1.518	1.356		0.893
1.518	1.435		0.945
1.518	1.383		0.911
		mean	0.917
		std dev	0.017

The time study results were compared with the 1X D.E.'s in the Analysis Table at the end of this report. The data in the Analysis Table represent samples which were analyzed immediately. Based on these results, dimethyl formamide is stable on silica gel for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.037$ $\overline{CV}_2 = 0.020$ $\overline{CV}_T = 0.056$

Data Sheet: Dimethyl Formamide S255

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.759	0.648	0.854	1.518	1.375	0.906	3.04	2.84	0.934
0.759	0.631	0.831	1.518	1.380	0.909	3.04	2.82	0.928
0.759	0.634	0.835	1.518	1.386	0.913	3.04	2.77	0.911
0.759	0.708	0.933	1.518	1.373	0.904	3.04	2.78	0.914
0.759	0.710	0.935	1.518	1.322	0.871	3.04	2.78	0.914
0.759	0.708	0.933	1.518	1.401	0.923	3.04	2.84	0.934
n =		6			6			6
mean		0.887			0.904			0.922
std dev		0.052			0.018			0.011
CV_1		0.059			0.020			0.012

$\overline{CV}_1$ 0.037

$\overline{CV}_{A+\overline{DE}}$ 0.040

The equation D.E. = $0.917 - e^{-4.96 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Dimethyl Formamide S255

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.390	0.505	47.8	10.57
	0.364	0.483	44.4	10.88
	0.355	0.477	45.7	10.44
	0.358	0.479	45.7	10.48
	0.352	0.474	44.4	10.68
	Sample was lost			
			n = 5	
			mean	10.61
			std dev	0.18
			CV_2	0.017
1S	0.864	0.957	40.9	23.4
	0.920	1.014	43.2	23.5
	0.926	1.021	44.4	23.0
	1.038	1.139	47.1	24.2
	0.935	1.031	43.8	23.5
	0.946	1.042	45.0	23.2
			n = 6	
			mean	23.5
			std dev	0.4
			CV_2	0.017
2S	2.69	2.93	47.8	61.3
	2.54	2.77	46.3	59.8
	2.41	2.63	44.4	59.2
	2.63	2.87	46.3	62.0
	Sample was lost			
	2.60	2.84	45.0	63.1
			n = 5	
			mean	61.1
			std dev	1.6
$\overline{CV}_2$ 0.020			CV_2	0.026

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387 (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Carbon Black, No. S262

OSHA Standard: 3.5 mg/cu m

Chemical Used for Validation: Vulcan XC 72, Cabot Corporation

Introduction

The method for carbon black, as well as some other compounds otherwise classified as nuisance dust, is gravimetric. Thus, the experimental studies with carbon black were done to include compounds with an OSHA standard equal to 15 mg/cu m in order to satisfy the experimental and statistical criteria, not only for carbon black but also for other analytes in the nuisance dust category.

The experimental work for gravimetric methods, and carbon black in particular, was done with a 25 mm, 2.0 micrometer PVC filter and filter holder with integral stainless steel support screen. This filter size was used because a 37 mm, 2.0 micrometer PVC filter was not available at the time. Since the time of the studies reported here, however, a 37 mm, 2.0 micrometer PVC filter has become available Therefore, use of a conventional 37 mm filter cassette assembly is recommended for these methods. The filters should be supported by a stainless steel support screen. The collection efficiency of this filter type and arrangement is expected to be the same and the use of a larger diameter filter will prevent overloading of the filter.

Procedure

The general procedure used is described in NIOSH Method No. S262 which is an adaptation of the filter collection of particulates except that for these particular validation studies, the analyte was collected on tared 25 mm, Type BS Millipore (2.0 micrometer pore size PVC) filters. The filters were dried to constant weight over Drierite for at least 12 hours, and weighed to determine the mass of sample collected. The recommended method is simply a gravimetric method and therefore the preparation of 18 analytical, or spiked, samples was omitted. However, the procedure was verified by the gravimetric analysis of 18 generated samples, 6 at each of the 0.5, 1 and 2X OSHA standard levels for a 200-liter sample. Gravimetric analyses were carried out with a Mettler M5 Microbalance. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method S262.

Modification

The filter recommended is 2.0 µm pore size polyvinyl chloride, 27 mm, instead of the 37 mm cellulose ester membrane filter because the latter tends to absorb moisture and is not suitable for gravimetric analysis.

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Generation

The basic system used to generate test atmospheres of carbon black is described in detail in Appendix A.

For the generation of each of the test levels studied, approximately one gram of carbon black powder was loaded and compressed lightly by hand into the dust holder. The concentration of the carbon black in the chamber was then controlled by proper adjustment of the dust holder advance rate. The system allows for the simultaneous collection of 12 samples; however, only 6 samples at each test level were collected and analyzed. Particulate atmospheres prepared in this manner using the Wright Dust Feeder normally produce particles in the respirable size fraction range. The average particle size of the Vulcan XC 72 carbon black was 0.03 microns. The sampling rate was 1.7 liters per minute. Since collection efficiency was found to be 1.00 ± 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. (Refer to Tables 1 and 2.) The range of atmospheric temperature and pressure during these studies were respectively 18-25°C and 749-761 mm Hg.

Discussion

The validation studies for carbon black were conducted in order to assess the gravimetric method not only for the analysis of carbon black but also for the analysis of other nuisance dusts as well, including boron oxide, and amorphous silica. Thus, the gravimetric analysis of carbon black was studied at 6 test concentration levels to simulate the equivalent of 0.5, 1 and 2X OSHA standard for carbon black (OSHA standard = 3.5 mg/cu m) using a 200-liter sample and a parallel equivalent for the nuisance dusts (OSHA standard = 15 mg/cu m) using a 100-liter sample. The sample volume tested in conjunction with these two OSHA standards was adjusted such that the sample size collected would represent a weighable amount of particulate but would minimize the danger of overloading the filter which can cause problems with the pump and also with sample flaking off the filter during handling and gravimetric analysis. The data for these samples are summarized in Tables 3 and 4.

The NIOSH recommended guidelines for the collection and gravimetric analysis of particulate have been to limit filter loadings to 2 mg/filter, in order to prevent handling losses. In order to prevent exceeding this value at the nuisance dust concentration levels, (Table 4), sampling should be restricted to 60 liters at 1 liter per minute. Sampling at these conditions would yield gravimetric data comparable to the weights in Table 3. Observe that the precision, $\overline{CV}_2$, for sample weights in the range of 0.4 - 1.6 mg (Table 3) is in excellent agreement with the precision of samples in the range of 0.8 - 2.9 mg (Table 4). The values were 0.0254 and 0.0258 respectively.

TABLE 1

Collection Efficiency: Carbon Black, S262

Generator Concentration: 6.3 mg/cu m
Sample Volume: 210 liters at 1.7 liters per minute

-------- µg Found ----------			
Front	Backup	Total	% Collected in Front
1332	13	1345	99.0
1307	22	1329	98.3
1322	14	1336	99.0
1349	44	1393	96.8
1321	15	1336	98.9
1228	- 2	1226	100.2

Average Collection Efficiency . . . 98.7%

TABLE 2

Collection Efficiency: Carbon Black, S262
For Nuisance Dust Levels, OSHA Standard = 15 mg/cu m

Generator Concentration: 28 mg/cu m
Sample Volume: 105 liters at 1.7 liters per minute

-------- µg Found ----------			
Front	Backup	Total	% Collected in Front
2858	0	2858	100.0
2909	2	2911	99.9
2970	- 1	2969	100.0
2885	4	2889	99.9
2892	- 1	2891	100.0
2990	- 6	2984	100.2

Average Collection Efficiency . . 100.0%

TABLE 3

Data Sheet: Carbon Black, S262
(25-mm PVC Filter)

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	401	213.5	1.878
	384	209.4	1.834
	414	208.2	1.988
	391	210.0	1.862
	382	213.2	1.792
	367	205.8	1.783
		n = 6	
		mean	1.856
		std dev	0.0746
		CV_2	0.0402
1S	710	212.5	3.34
	701	213.5	3.28
	685	208.2	3.29
	725	214.4	3.38
	703	210.0	3.35
	708	213.2	3.32
		n = 6	
		mean	3.33
		std dev	0.0378
		CV_2	0.0113
2S	1620	210.7	7.69
	1595	211.9	7.53
	1644	212.6	7.73
	1601	204.7	7.82
	1630	208.8	7.81
	1627	210.9	7.71
		n = 6	
		mean	7.71
		std dev	0.1050
		CV_2	0.0136
		$\overline{CV}_2$	0.0254

TABLE 4

Data Sheet: Carbon Black, S262
For Nuisance Dust Levels, OSHA Standard = 15 mg/cu m

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	785	105.6	7.43
	847	106.1	7.98
	829	104.1	7.96
	822	103.5	7.94
	854	106.6	8.01
	812	106.0	7.66
		n = 6	
		mean	7.83
		std dev	0.2336
		CV_2	0.0298
1S	2299	114.9	20.01
	2232	110.5	20.20
	2153	112.7	19.10
	2267	112.3	20.19
	2191	113.1	19.37
	2279	113.9	20.01
		n = 6	
		mean	19.81
		std dev	0.463
		CV_2	0.0234
2S	2858	105.8	27.01
	2909	106.4	27.34
	2970	102.7	28.92
	2885	104.8	27.53
	2892	104.4	27.70
	2990	107.3	27.87
		n = 6	
		mean	27.73
		std dev	0.655
		CV_2	0.0236
		$\overline{CV}_2$	0.0258

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Collection Efficiency

Two sets of 6 generated samples collected on 25-mm Type BS Millipore filters were used for these studies. One set of samples represents a test atmosphere concentration of 6.3 mg/cu m sampled at 1.7 liters per minute for 120 minutes (210 liters) and the other is for a concentration of 28 mg/cu m sampled at 1.7 liters per minute for 60 minutes (105 liters). The front and backup filters were arranged in the 25-mm filter cassette holder such that the two filters were mounted back to back and in contact with each other; the filters were supported by a 25-mm, stainless steel screen. The average collection efficiencies were 99% and 100% respectively for the test atmospheres containing 6.3 mg/cu m and 28 mg/cu m. (Refer to Tables 1 and 2.)

Precision and Accuracy

The statistical procedures are described in Reference 1; calculations were based on the data summarized in Tables 3 and 4.

For carbon black, OSHA standard = 3.5 mg/cu m.

$$\overline{CV}_2 = 0.0254 \qquad \overline{CV}_T = 0.0561$$

For nuisance dust, OSHA standard = 15 mg/cu m.

$$\overline{CV}_2 = 0.0258 \qquad \overline{CV}_T = 0.0563$$

Since the collection efficiency was found to be at least 99%, the values found also represent the generator concentration. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Appendix A

Description of Dust Atmosphere Generation Apparatus

The basic elements of the system used to generate the dust test atmospheres are shown in Figures 1 and 2. The system consists of a Wright Dust Feeder, an aerosol charge neutralizer, and an 80-liter stainless dust chamber.

Dust samples to be dispersed in the apparatus are compressed into a container which is attached to the Wright Dust Feeder. In operation, the container and the dust compact are slowly rotated and driven against a stationary scraper blade by an electrically-operated mechanism. The blade continuously removes dust from the compact surface at a uniform rate. Compressed air enters the container and entrains the dust particles. The dust holder advance rate may be varied by changing the gears in the drive mechanism to provide a wide range of dust concentrations.

A short distance downstream of the dust feeder there is an auxiliary port for introducing additional air for further dilution of the dust cloud. Normally, a flow of 30 liters per minute is passed through the dust feeder itself, and dilution air is added at the rate of 70 liters per minute. Air flow rates are read from calibrated rotameters. Compressed air is supplied to the apparatus from the house compressed air system. This air is dried by passing it through a silica gel bed and then through a high efficiency fibrous filter and a membrane filter to remove particulate matter.

Since dust particles may accumulate electric charges in the dispersal process, the dispersed dust is passed through a charge neutralizer (Thermo-Systems Incorporated, Model 3045) before it is introduced into the dust chamber. The active element of the neutralizer is a 10 millicurie krypton-85 beta source. Beta rays from the krypton-85 interact with air molecules to generate both positive and negative ions. The ions become attached to the dust particles of opposite charge.

The dust chamber itself was constructed from two stainless steel stock pots. The pots are held together by three latches. An O-ring is used to provide an air-tight seal between the two pots. The chamber diameter is 14 inches and its height is 32 inches. Baffles were placed at the entrance and exit of the dust chamber to promote uniform distribution of the aerosol. The baffles are 5.75 inches in diameter, 0.015 inches thick, and are located approximately 1.5 inches away from the exit and entrance ports. The dust chamber is normally operated at a slight positive pressure with respect to the atmosphere (about 2 inches of H_2O). Effluent from the dust chamber is vented to a hood through a one-inch rubber hose.

Twelve sampling ports are located around the periphery of the dust chamber. The filter cassettes are mounted on the inside perimeter of the chamber, and sample flow rate is controlled by critical orifices which are mounted outside the chamber on a U-shaped vacuum line (see Figure 2). The sampling rate is approximately 1.7 liters per minute.

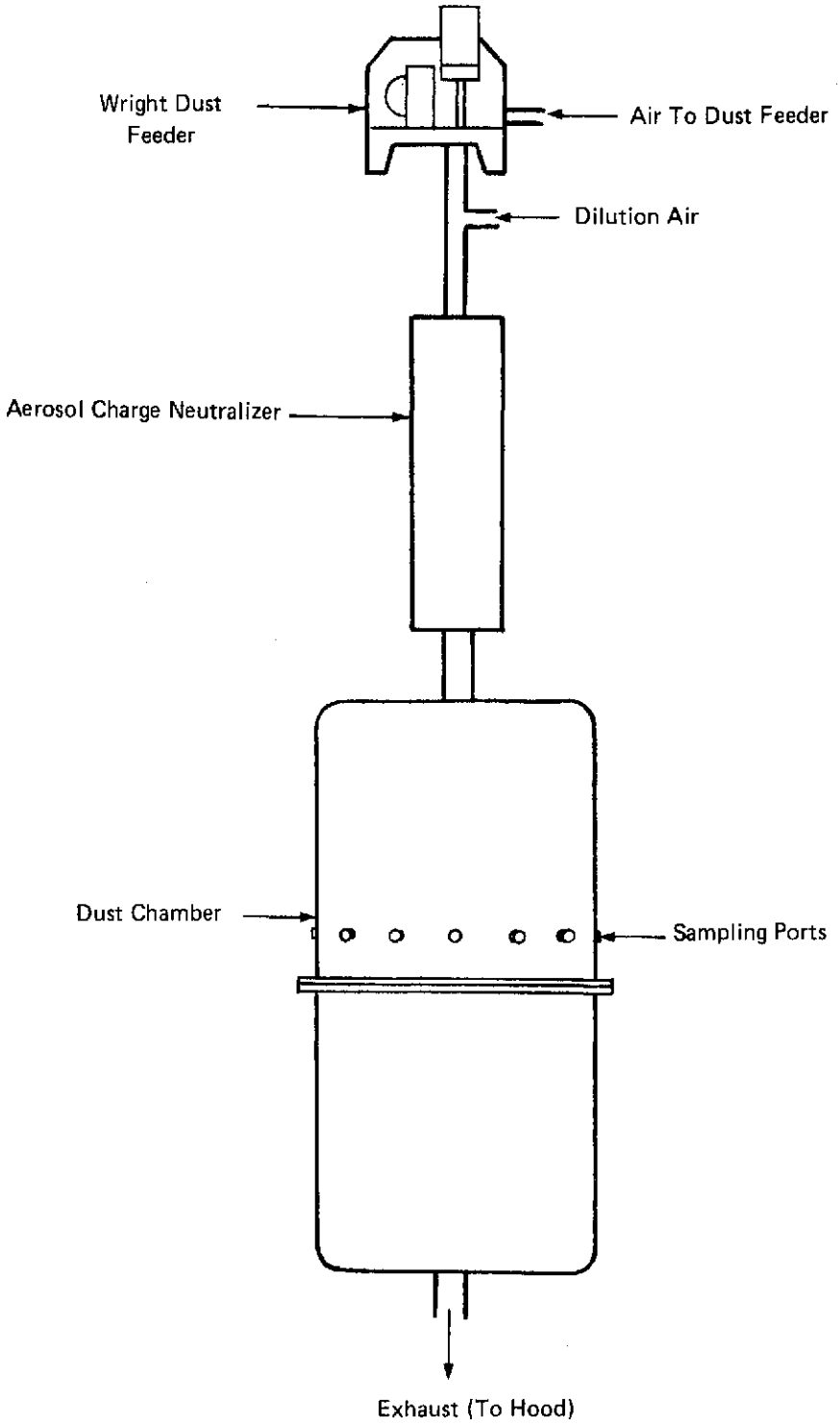

FIGURE 1 DUST GENERATION APPARATUS

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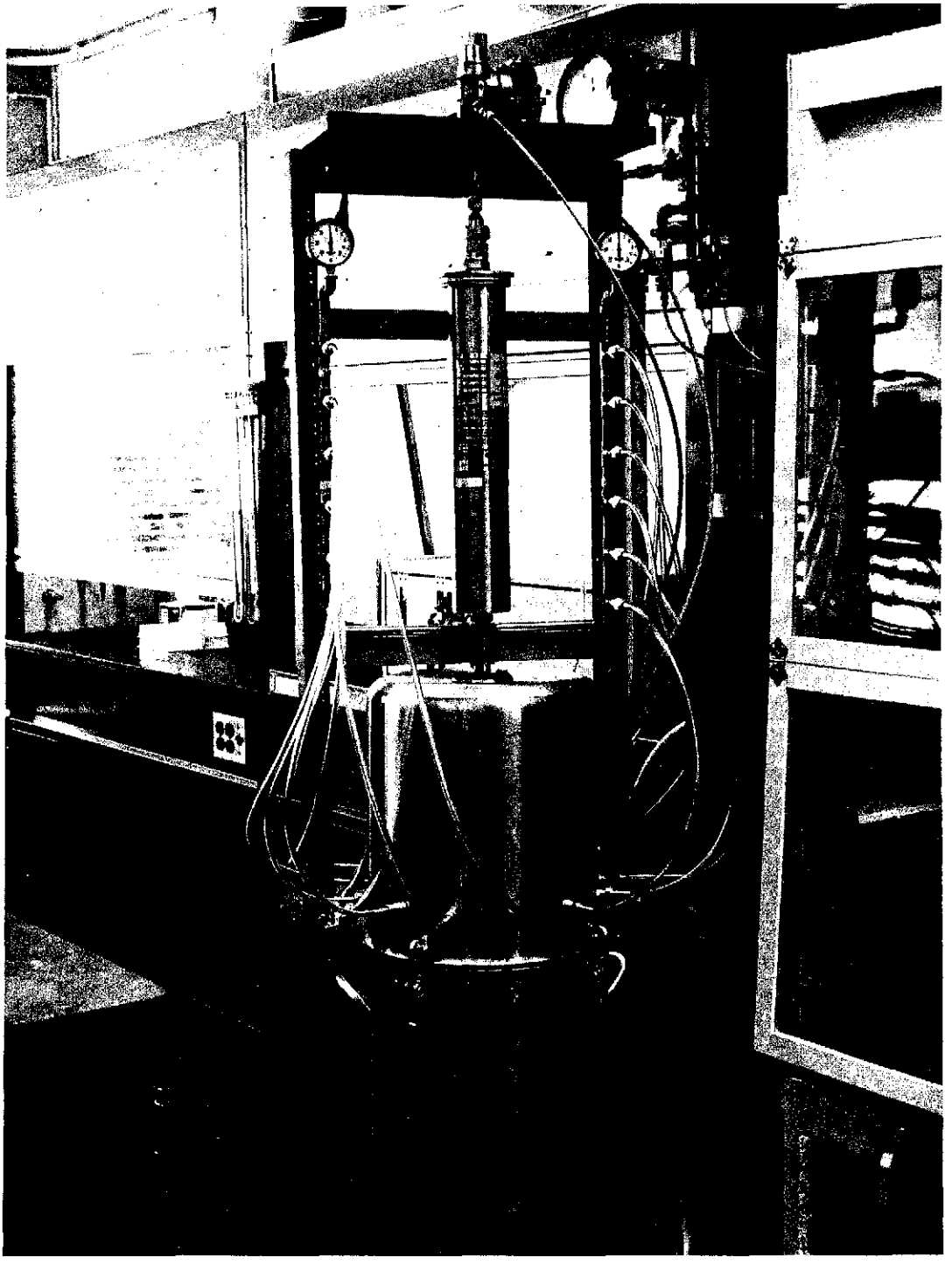

FIGURE 2 PHOTOGRAPH OF DUST GENERATION APPARATUS

Backup Data Report

Substance: Ethyl Silicate, No. S264

OSHA Standard: 850 mg/cu m

Chemical Used for Validation: Tetraethyl Orthosilicate, Eastman Organic Chemicals

Procedure

The general procedure developed is described in detail in NIOSH Method No. S264. The ethyl silicate in air was collected by drawing 9 liters of air through a glass tube containing 100 mg of XAD-2 resin in the front section and 50 mg in the backup section. The ethyl silicate was desorbed from the resin with carbon disulfide and analyzed using a gas chromatograph equipped with a flame ionization detector. Desorption efficiency tests were done by spiking with the appropriate volume of ethyl silicate such that the amount added was equivalent to that present in a 9-liter air sample at 0.5, 1 and 2X OSHA standard. The resin used was XAD-2 supplied by Rohm and Haas, Philadelphia, PA. Spiking and desorption tests were done in 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Descriptive details of the instrumentation used may be found in the Butyl Acetate S47 Backup Data Report and attachment.

Modification

The method recommended for ethyl silicate as NIOSH Method S264 utilizes XAD-2 resin as the collection medium instead of charcoal. This substitution was devised because the desorption efficiency from charcoal was low. The charcoal studies were conducted by preparing duplicate spiked samples using Lot 105 charcoal and testing the desorption efficiency with selected solvents. Samples were spiked at two concentration levels, equivalent to the amount present in a 10- and 25-liter sample at the OSHA standard. The average desorption efficiency with carbon disulfide at both levels was low and similar low values were obtained with the other solvents as shown below.

Solvent	mg added	Desorption Efficiency
Carbon Disulfide	8.4	0.64
Methanol	8.4	0.28
Chloroform	8.4	0.68
Ethyl Acetate	8.4	0.65
Carbon Disulfide	21.5	0.71
Chloroform	21.5	0.74

Also, the desorption efficiency from Lot 104 charcoal was found to be lower than the DE's from Lot 105; the average DE found was 0.39 for samples spiked with 8.4 mg and desorbed with carbon disulfide.

Generation

The data for two sets of 18 generated samples are presented. Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering ethyl silicate via a syringe injector into a stream of dry air. For the first set of samples noted, ethyl silicate was delivered at the rate of 159.7 mg/min into the air stream flowing at the rate of 0.0986 cu m/min, while for the second set the rates were respectively 160.9 mg/min and 0.100 cu m/min. In each case, the three sample lines were maintained at dilution ratios of 0.233, 0.486 and 1.000 to produce the corresponding 0.5, 1 and 2X OSHA standard test levels. All six samples at the three test levels were collected simultaneously at 0.067 liter per minute for 135 minutes (9 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

In the search for a suitable collection media, the capacity of several solid sorbents for ethyl silicate was determined at test levels equal to 2X OSHA standard and a sampling rate of 0.8 liter per minute. The data are summarized below.

Solid Sorbent	Test Level mg/cu m	Capacity at 5% Breakthrough	
		Liters	mg
Lot 105 Charcoal	1720	17	29
Lot 104 Charcoal	1720	23	39
Chromosorb 102	1640	9	15
XAD-2	1640	15	24

Discussion

The sample volume tested was based on the rule that the sample size should be 2/3 the 5% breakthrough capacity at the 2X OSHA standard test level. Thus, a 9-liter sample size has been used for all studies. The backup sections of the generated samples at the 2X standard test level were analyzed in each case. The collection efficiency data summarized in Table 1 for the two sets of samples generated show that only a small amount of ethyl silicate breaks through for the 9-liter samples collected at 0.067 liter per minute. The average collection efficiency found was 98%. These data suggest that the specifications on flow rate and sample volume must be followed closely.

Studies to determine effect of storage on sample stability showed that the average desorption efficiency for 1-day-old samples was 0.96 as compared with 0.94 for 5-days-old samples as shown in Tables 2 and 3. The generated samples also show no significant difference in recovery for 1-day-old vs. 4-days-old samples as shown in Table 5 where the first three samples for each test level represent fresh samples while the rest were stored for 4 days. Note that the appropriate DE values were used to determine the corrected mg.

It should be noted that some mechanical handling problems were encountered in the process of transferring the samples freshly collected on XAD-2 resin into the desorption vials. It appears that some buildup of electrostatic charge occurs during the sample collection process (probably due to the fact that dry air was used in the sample generation), thus making the resin particles tend to hang on to the walls of the glass tube. This handling problem was not encountered in the stored samples. The actual cause of the charge buildup is unknown presently, but based on the experimental observations gathered during the validation program a note on how to dissipate the charge for easier sample handling is included in the NIOSH Method S264.

Precision and Accuracy

The statistical procedures used are described in Reference 1. The statistical calculations were performed on the samples which had been stored.

$\overline{CV}_1 = 0.0096$ $\overline{CV}_2 = 0.0253$ $\overline{CV}_T = 0.0562$

The average recovery of the generated samples over all levels for the two sets of samples collected was 90.8%. Refer to Tables 4 and 5.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Collection Efficiency on XAD-2 of Ethyl Silicate, No. S264

mg Found[Δ]			
Front	Backup	Total	% Collection Efficiency[(1)]
13.03	0.187	13.22	98.6
12.40	0.766	13.17	94.2
13.28	0.282	13.56	97.9
12.53	0.236	12.77	98.2
12.46	0.061	12.52	99.5
12.80	0.320	13.12	97.6
12.23	0.000	12.23	100.0
12.11	0.465	12.58	96.3
11.90	0.288	12.19	97.6
0.89*	-	-	-
11.47	0.099	11.57	99.1
11.81	0.189	12.00	98.4

Average Collection Efficiency...97.9

[Δ]Corrected for appropriate DE value.

*This value has been excluded.

[(1)]For a sample size of 9 liters at a rate of 0.067 liter per minute.

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TABLE 2

Data Sheet: Ethyl Silicate, S264
(Samples Stored for 1 day)

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.85	3.55	0.922	7.63	7.25	0.950	15.04	14.34	0.953
3.85	3.61	0.938	7.63	7.27	0.953	15.04	14.66	0.975
3.85	3.71	0.964	7.63	7.30	0.957	15.04	14.56	0.968
3.85	3.62	0.940	7.63	7.36	0.965	15.04	14.41	0.958
3.85	3.84	0.997	7.63	7.23	0.948	15.04	14.37	0.955
3.85	4.02	1.044	7.63	7.73	1.013	15.04	14.38	0.956
n =		6			6			6
mean		0.968			0.964			0.961
std dev		0.0457			0.0246			0.0087
CV_1		0.0472			0.0255			0.0090

$\overline{CV_1}$ 0.0314

$\overline{CV}_{A+\overline{DE}}$ 0.0339

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TABLE 3

Data Sheet: Ethyl Silicate, S264
(Samples stored for 5 days)

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.89	3.60	0.925	7.71	7.23	0.938	15.28	14.51	0.950
3.89	3.51	0.902	7.71	7.23	0.938	15.28	14.59	0.955
3.89	3.56	0.915	7.71	7.17	0.930	15.28	14.26	0.933
3.89	3.60	0.925	7.71	7.29	0.946	15.28	14.60	0.955
3.89	3.61	0.928	7.71	7.24	0.939	15.28	14.65	0.959
3.89	3.63	0.933	7.71	7.27	0.943	15.28	14.56	0.953
n =		6			6			6
mean		0.921			0.939			0.951
std dev		0.0111			0.0054			0.0092
CV_1		0.0121			0.0058			0.0097

$\overline{CV_1}$ 0.00956

$\overline{CV_{A+\overline{DE}}}$ 0.0103

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TABLE 4

Data Sheet: Ethyl Silicate, S264
(Samples stored for 5 days)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.84	3.09	8.79	352	377	
	2.82	3.07	8.67	354	377	
	2.94	3.20	9.15	350	377	
	3.02	3.28	9.41	349	377	
	3.00	3.26	9.48	344	377	
	2.76	3.00	9.28	323	377	
			n = 6			
			mean	345		0.915
			std dev	11.45		
			CV_2	0.0332		
1S	6.14	6.53	8.91	733	787	
	6.02	6.40	8.79	728	787	
	6.04	6.43	8.79	732	787	
	5.96	6.34	8.55	742	787	
	5.92	6.30	8.67	727	787	
	5.90	6.28	8.67	724	787	
			n = 6			
			mean	731		0.929
			std dev	6.32		
			CV_2	0.0087		
2S	11.62	12.23	8.55	1430	1620	
	11.94	12.57	8.67	1450	1620	
	11.57	12.18	8.79	1386	1620	
	0.84*	-	8.80	-	1620	
	10.99	11.57	8.55	1353	1620	
	11.40	12.00	8.67	1384	1620	
			n = 5			
			mean	1401		0.865
			std dev	38.9		
			CV_2	0.0278		
			$\overline{CV}_2$	0.0253		

*These values excluded from statistical analysis

TABLE 5

Data Sheet: Ethyl Silicate, S264
(Samples stored for 1 and 4 daysΔ)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.90	3.02	8.93	338	374	
	2.98	3.10	8.81	352	374	
	3.10	3.23	9.29	348	374	
	3.06	3.33	9.56	348	374	
	3.08	3.35	9.63	348	374	
	2.86	3.11	9.42	330	374	
			n = 6			
			mean	344		0.920
			std dev	8.29		
			CV_2	0.0241		
1S	6.10	6.35	9.05	702	781	
	6.00	6.25	8.93	700	781	
	6.08	6.33	8.93	709	781	
	*	*	8.69	*	781	
	5.98	6.36	8.81	722	781	
	5.92	6.30	8.81	715	781	
			n = 5			
			mean	710		0.909
			std dev	9.13		
			CV_2	0.0129		
2S	12.56	13.08	8.69	1505	1607	
	12.51	13.03	8.81	1479	1607	
	12.89	13.43	8.93	1504	1607	
	12.12	12.76	9.42	1355	1607	
	11.90	12.53	8.69	1442	1607	
	12.46	13.12	8.81	1489	1607	
			n = 6			
			mean	1462		0.910
			std dev	57.4		
			CV_2	0.0393		
			$\overline{CV}_2$	0.0284		

*These values excluded from statistical analysis
ΔThe first three samples of each set were stored for one day.

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Backup Data Report

Substance: Oil Mist, Mineral, No. S272

OSHA Standard: 5.0 mg/cu m

Chemical Used for Validation: Machine Cutting Oil, Gulf Oil Company

Procedure

The general procedure used is described in NIOSH Method No. S272 which is an adaptation of P&CAM 159 for the collection and analysis of oil mist in air. The reliability of the analytical method was tested at sample concentrations equivalent to the levels present in a 100-liter sample at 0.5, 1 and 2 times the OSHA standard. The analytical samples were prepared by adding the appropriate aliquot of a standard solution of the analyte in chloroform to 37-mm Type AA Millipore filters; a set of 18 analytical samples, 6 at each test level, was prepared. The samples were extracted with 10-ml of spectroquality chloroform (Burdick and Jackson) and analyzed by fluorescence spectrophotometry. Analyses were done with a Hitachi Perkin-Elmer Model MPF 44. For the oil sample used for this validation study, fluorescence measurements were obtained using the following instrument settings:

Excitation wavelength	- 307 nm
Excitation slit width	- 4.5 nm
Emission wavelength	- recorded from 300-420 nm with peak maxima at 360 nm
Emission slit width	- 4 nm
Filter	- none

The fluorescence intensity was used as a measure of oil concentration in the sample. Appropriate standard solutions were analyzed at the same time the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S272.

Modification

There was no major modification of P&CAM 159 except that 10 ml of chloroform, instead of 5 ml, was used for extraction because of the strong fluorescence of the oil sample tested, i.e., the fluorescence intensity over the desired concentration range was non-linear when 5 ml of chloroform was used.

It should also be noted that a sample of paraffin oil and a commercial brand of mineral oil (McKesson) were obtained and tested at a concentration of 100 µg/ml; no fluorescence was detected in either of these

oil samples. Subsequently a sample of vacuum pump oil and the Gulf cutting oil were tested; both of these oil samples emitted strong, multiple peaks over the wavelength range of 300-400 nm. The Gulf cutting oil was used for the validation study.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by direct atomization of Gulf cutting oil. The system used for the generation of test atmospheres of oil mist was the same unit as that used for the triphenyl phosphate and is described in the S210 Triphenyl Phosphate Backup Data Report; the basic components of this generator are reproduced again in Figures 1 and 2. Approximately 200-300 ml of cutting oil was added to the 500-ml three-neck round-bottom flask. The liquid was nebulized by passing a regulated amount of air through the Laskin nozzle (Figure 1); the air-flow through the nozzle and the dilution air flow through the dilution tube were adjusted and balanced until the desired mainline concentration was produced. The other components of the generation/dilution system are described in detail in the S97 Octachloronapththalene Backup Data Report and Attachment. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5X the OSHA standard level. A set of 18 samples, 6 at each of the three test levels, was collected simultaneously at 1.5 liters per minute for 66 minutes (100 liters) at 22°C and 755 mm Hg atmospheric temperature and pressure.

Collection Efficiency

To determine the collection efficiency of the 37-mm Type AA Millipore filter for oil mist, two filters were mounted in the three-piece filter cassette such that the front and backup filters were physically separated and only the backup filter was supported by the cellulose backup pad. Six such sample filter cassettes were used to determine the collection efficiency for an air sample concentration of 11.7 mg/cu m at a sampling rate of 1.5 liters per minute for 66 minutes. Each filter was analyzed separately and the relative amount of oil mist collected in the primary and backup filters was determined, based on the total quantity found in both filters. The data summarized in Table 1 show that the average collection efficiency for oil mist was 100%.

Precision and Accuracy

The statistical procedures used are described in Reference 1; the data used for calculations are shown in Tables 2 and 3.

$\overline{CV}_1 = 0.0255$ $\overline{CV}_2 = 0.0403$ $\overline{CV}_T = 0.065$

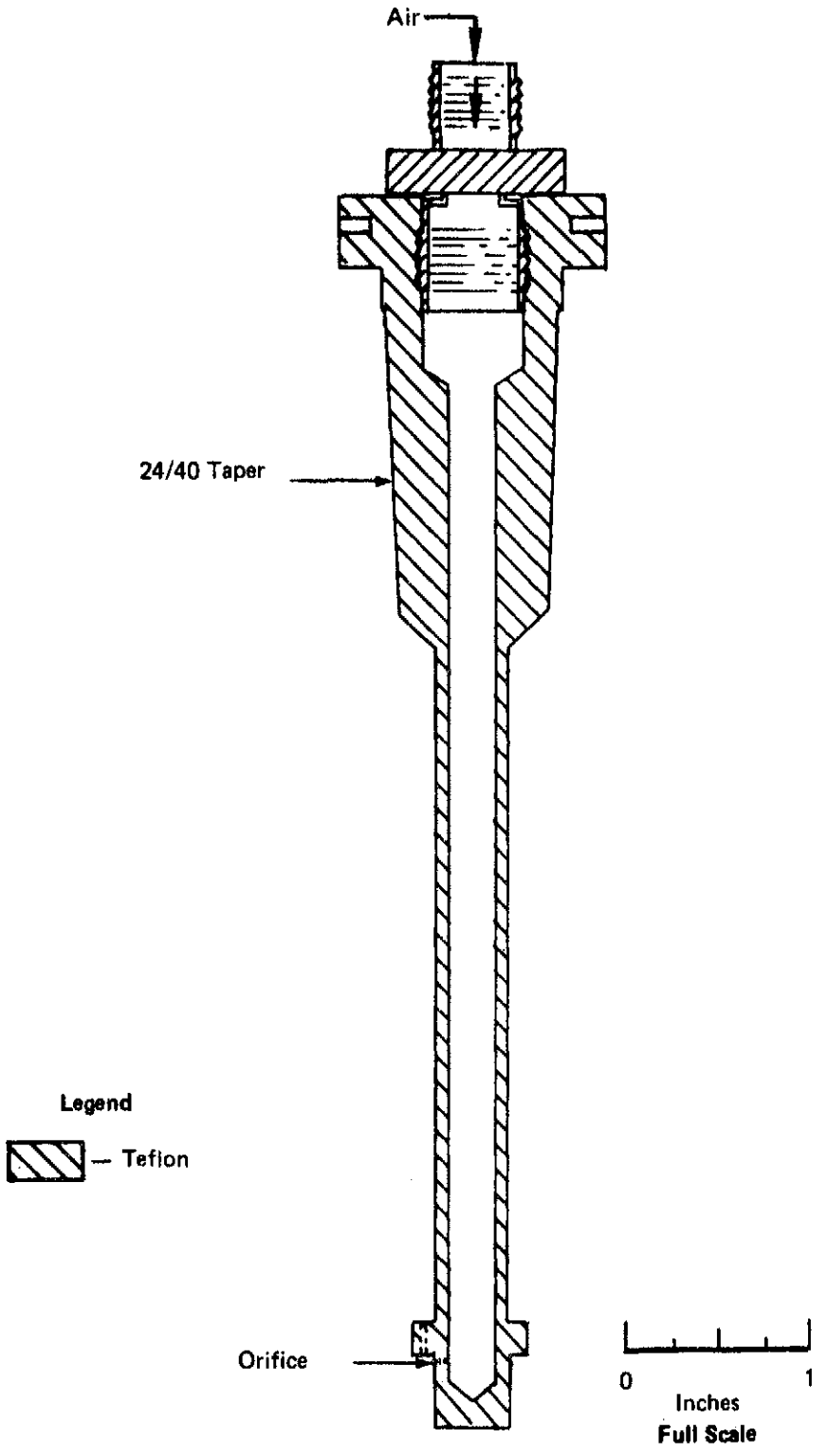

FIGURE 1 CROSS SECTIONAL VIEW OF LASKIN TYPE NOZZLE

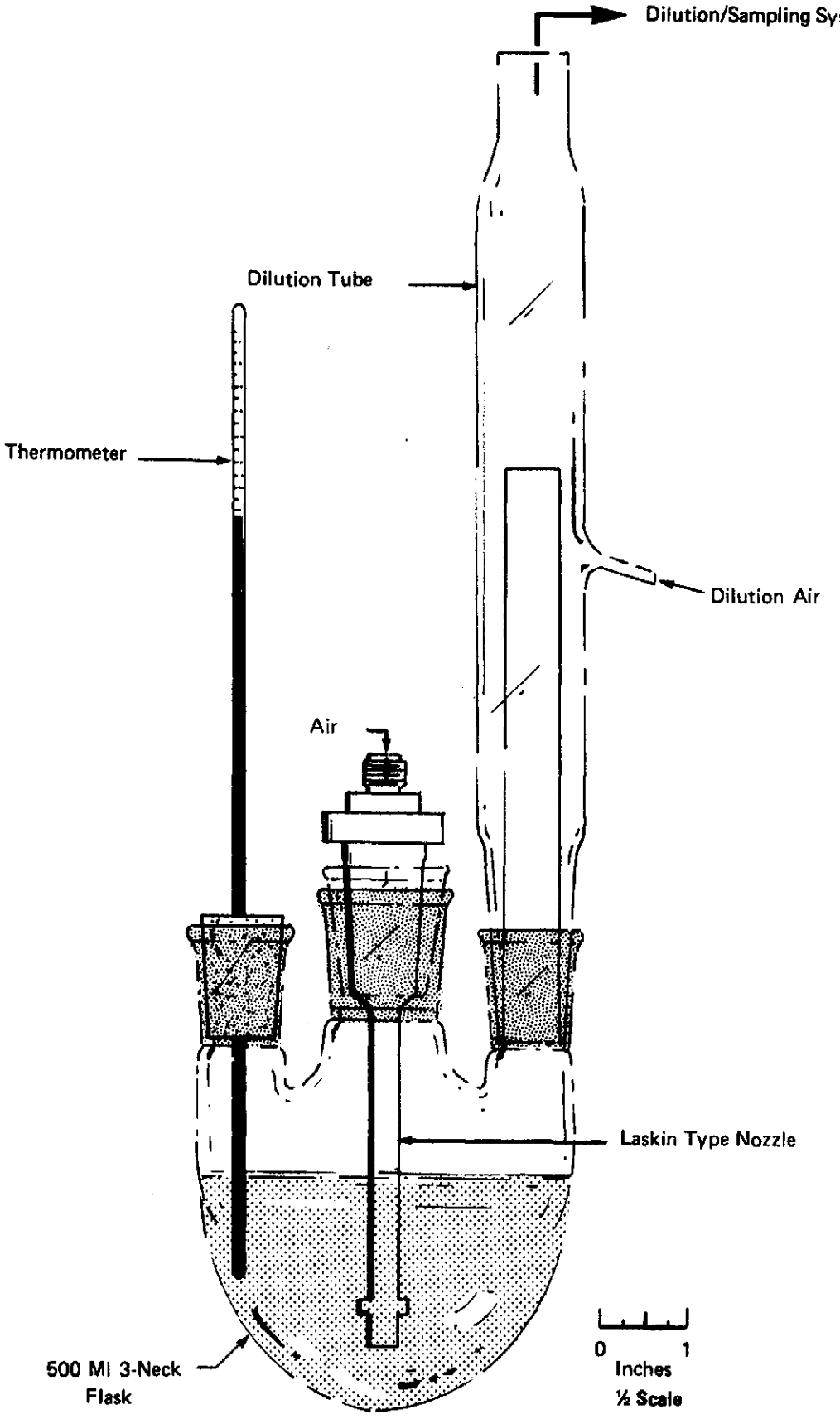

FIGURE 2 CROSS-SECTIONAL VIEW OF NEBULIZER/DILUTION SYSTEM

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TABLE 1

Collection Efficiency of Oil Mist on
Type AA Millipore Filters

µg Found			% Collected
Front	Backup	Total	in Front
1160	ND	1160	100
1160	ND	1160	100
1130	ND	1130	100
1130	ND	1130	100
1290	ND	1290	100
1230	ND	1230	100

Average Collection Efficiency 100%

ND - not detectable; the lower limit of detection for the cutting oil used for these validation studies was 10 µg in 10 ml of chloroform.

Since the collection efficiency was found to be 100% and no bias was found in the analytical recovery studies, average recovery = 97.7%, $\overline{CV}_T$ is a satisfactory measure of both precision and accuracy.

Reference

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 2

Data Sheet: Oil Mist, S272
(37-mm Type AA Millipore Filters)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
250	240	0.960	500	502	1.004	1000	1010	1.010
250	240	0.960	500	495	0.990	1000	980	0.980
250	240	0.960	500	502	1.004	1000	965	0.965
250	245	0.980	500	500	1.000	1000	980	0.980
250	240	0.960	500	495	0.990	1000	1020	1.020
250	230	0.920	500	460	0.920	1000	980	0.980
n =		6			6			6
mean		0.957			0.985			0.989
std dev		0.0197			0.0323			0.0211
CV_1		0.0206			0.0328			0.0213

$\overline{CV}_1$ 0.0255

$\overline{CV}_{A+\overline{DE}}$ 0.0276

TABLE 3

Data Sheet: Oil Mist, S272

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m
0.5S	250	101.4	2.465
	260	101.0	2.574
	250	100.6	2.485
	250	101.2	2.470
	250	100.9	2.478
	275	101.8	2.701
		n = 6	
		mean	2.529
		std dev	0.0935
		CV_2	0.0370
1S	605	101.5	5.96
	620	101.6	6.10
	600	101.1	5.93
	605	101.9	5.94
	605	102.3	5.91
	640	101.8	6.29
		n = 6	
		mean	6.02
		std dev	0.1480
		CV_2	0.0246
2S	1160	101.5	11.43
	1160	101.4	11.44
	1130	101.4	11.14
	1130	101.4	11.14
	1290	101.2	12.75
	1230	102.2	12.04
		n = 6	
		mean	11.66
		std dev	0.628
		CV_2	0.0539
		$\overline{CV}_2$	0.0403

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Backup Data Report

Substance: Carbaryl (Sevin), No. S273

OSHA Standard: 5 mg/cu m

Chemical Used for Validation: Carbaryl (Sevin), Anal. Grade
Union Carbide, Salinas, California

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S273. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 90-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (5, 10, and 20 microliters) of a 460 mg/10 ml solution of carbaryl in dichloromethane were spiked onto 37-mm glass fiber filters. Methanolic potassium hydroxide was used to remove the analyte from the filter and to hydrolyze it. Subsequent reaction with p-nitrobenzenediazonium fluoroborate resulted in a colored reaction product. The absorbance of the colored product was read at 475 nm and used as a quantitative measure of the amount of carbaryl. Details of the analytical procedure may be found in Section 8.4 of NIOSH Method No. S273.

Test atmospheres of carbaryl at each of the three levels of 0.5X, 1X and 2X the OSHA standard were generated as discussed below. Six samples at each of the three concentrations were collected on Type A glass fiber filters. In the laboratory validation study, a backup pad was not used, however it is recommended that one should be used for field sampling.

Generation

Samples of carbaryl in air were generated by the procedure described in Reference No. 1. A commercially available formulation of Sevin ("49-er Gold Strike Sevin 15" labelled as containing 15% by weight of carbaryl and 85% by weight of inert ingredients) was used for generation. This material was diluted in toluene to obtain a mixture of 4.3% carbaryl, which was determined by analyzing the mixture. An aerosol of carbaryl was generated from this solution using the techniques described in Reference No. 1. A Thermo Systems particle mass monitor was used to establish generation conditions as described in Reference No. 2.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples were collected for at least ten minutes, and these samples were analyzed. These results were used to select conditions that would give the desired concentration in the generator. When the desired concentration was obtained, six samples at each of the three levels were collected simultaneously using the three stage dilution system described in Reference No. 3. Samples were collected for one hour of approximately 1.5 liters per minute.

Collection Efficiency

Collection efficiency tests were conducted at 13.4 mg/cu m (as determined by analysis of samples collected at 2X the OSHA standard level) by mounting in series two filters in direct contact with each other. The results of the collection efficiency test are given below:

mg/cu m first filter	mg/cu m backup filter	Collection Efficiency
13.5	N.D.*	1.00
13.3	"	1.00
13.5	"	1.00
13.4	"	1.00
13.5	"	1.00

* N.D. = Not detected at a detection limit of 0.1 mg/cu m.

(Solutions from the backup filters were read in a 5-cm cell.)

Since collection efficiency was determined to be 1.00, no correction for collection efficiency is needed in this method.

Storage Stability Study

A test was done to ascertain whether collected samples could be stored without loss of the analyte. Six glass fiber filters were each spiked with 0.460 mg of carbaryl. These samples were then placed in screw top jars fitted with Teflon-lined caps, and stored on the laboratory bench top for six days before analysis. The results are presented below:

STORAGE STABILITY TEST
(Samples stored six days)

	mg		
Sample	taken	found	Recovery
1	.460	.483	1.05
2	.460	.471	1.02
3	.460	.472	1.03
4	.460	.471	1.02
5	.460	.467	1.02
6	.460	.463	1.01

The average recovery of 1.02 for these samples indicate that the collected samples can be stored for at least six days without loss. The results of this test were compared with the results of samples which were analyzed the day after spiking. The A.M.R.s of the one-day old samples are given in the Analysis table at the end of this report.

Discussion

It was not known at the onset of the laboratory studies whether carbaryl would exist as a particulate, vapor, or a combination of both over the range of concentrations tested. A preliminary test was conducted to determine if the analyte would remain on a glass fiber filter (cellulose ester filters were not chosen, because they are not inert in glacial acetic acid which was used in the analysis). Four filters were spiked with the amount of carbaryl which would be collected at 2X the OSHA standard level. Two of these filters were placed in filter cassettes and 90 liters of air were sampled through them. The other two filters were unsampled. The results of the analysis of these filters are as follows:

	mg added	mg found	Recovery
Filter #1--90 liters of air drawn through	0.920	0.938	1.02
Filter #2--90 liters of air drawn through	0.920	0.944	1.03
Filter #3--unsampled	0.920	0.940	1.02
Filter #4--unsampled	0.920	0.960	1.04

This test indicated that the analyte would be present as a particulate since no material was lost from the sampled filters. Thus, collection on a filter seemed appropriate.

More conclusive tests on vapor contribution were performed on generated samples.

A set of samples was generated using the same method as used for the set of samples taken for validation. Samples were collected on glass fiber filters followed by a midget bubbler containing 10 ml of 0.1 M potassium hydroxide in methanol. Any vapor passing through the filter would be collected in the bubbler. The flow rate and sampling time were the same as those used during validation. The filters and bubblers were analyzed separately.

The filters were analyzed as described above. The bubblers were analyzed by bringing the volume in the bubbler to 20 ml with the collecting medium, and 18 ml of the resulting solution was used for analysis. To this solution 17 ml of glacial acetic acid was added, and then 1 ml of p-nitrobenzenediazoniumfluoroborate solution was added. Absorbance was read at 475 nm, using a 5-cm cell. This modified method was checked by spiking 9.2 μg of carbaryl into 18 ml of methanolic KOH and analyzed as above. Four samples were prepared and gave absorbances of 0.20, 0.18, 0.19, and 0.17 in the 5-cm cell. The results of the test are given below:

TEST FOR VAPOR CONTRIBUTION OF GENERATED SAMPLES

	mg/cu m found	
Sample	Filter	Backup Bubbler
1	15.2	< .11
2	16.1	< .11
3	16.4	< .11
4	15.0	< .11
5	16.0	< .12

These results are in agreement with the preliminary results obtained on the spiked filters, and support the use of a filter for collection of carbaryl, as opposed to the use of a filter and bubbler combination.

Precision and Accuracy

The statistical procedures are described in Reference No. 4.

$\overline{CV}_1 = 0.015$ $\overline{CV}_2 = 0.027$ $\overline{CV}_T = 0.057$

Data Sheet: Carbaryl S273

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.2300	0.2337	1.016	0.460	0.468	1.017	0.920	0.986	1.072
0.2300	0.2293	0.997	0.460	0.458	0.996	0.920	0.971	1.055
0.2300	0.2346	1.020	0.460	0.452	0.983	0.920	0.977	1.062
0.2300	0.2302	1.001	0.460	0.451	0.980	0.920	0.961	1.045
0.2300	0.2293	0.997	0.460	0.457	0.993	0.920	0.970	1.054
0.2300	0.2239	0.973	0.460	0.453	0.985	0.920	0.943	1.025
n =		6			6			6
mean		1.001			0.992			1.052
std dev		0.017			0.014			0.016
CV_1		0.017			0.014			0.015

$\overline{CV}_1$ 0.015

$\overline{CV}_{A+\overline{AMR}}$ 0.016

Data Sheet: Carbaryl S273

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.1845	90.0	2.050
	0.1802	95.5	1.887
	0.1760	90.5	1.945
	0.1802	92.7	1.944
	0.1802	91.7	1.965
	0.1743	88.7	1.965
		n = 6	
		mean	1.959
		std dev	0.053
		CV_2	0.027
1S	0.365	92.0	3.97
	0.376	89.8	4.19
	0.395	89.8	4.40
	0.381	90.9	4.19
	0.366	90.9	4.03
	0.386	90.9	4.25
		n = 6	
		mean	4.17
		std dev	0.15
		CV_2	0.036
2S	1.271	94.0	13.52
	1.247	94.0	13.27
	1.252	92.8	13.49
	1.169	87.3	13.39
	1.148	85.3	13.46
	Sample was lost.		
		n = 5	
		mean	13.43
		std dev	0.10
$\overline{CV}_2$ 0.027		CV_2	0.007

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Trichloronaphthalene, No. S128, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: DDT [2,2-bis (p-chlorophenyl)-1,1,1-trichloroethane], No. S274

OSHA Standard: 1.0 mg/cu m - skin

Chemical Used for Validation: DDT, analytical reagent Shell

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S274. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 90-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of a 22.5 micrograms/microliter solution of DDT in a benzene/iso-octane solution (1:5) were spiked onto 37-mm glass fiber filters. The analyte was extracted from the filters with 15 ml of iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S274.

Test atmospheres of DDT at concentrations of approximately 0.5X, 1X, and 2X the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type AE glass fiber filters.

Generation

Samples of DDT in air were generated by the procedure described in Reference No. 1. However, the system was modified by installing a secondary cyclone to further maintain the proper particle size distribution. A 5% solution of DDT in paint thinner (by weight) was prepared to represent commercial fly spray formulation. This solution was used to prepare a 0.5% solution of DDT in toluene (100 ml of the 5% solution of DDT in paint thinner made up to a 1-liter volume in toluene) for the generation of test atmospheres of DDT.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples collected for at least ten minutes, and these samples analyzed. The results of the analyses were used to select conditions to reach the required concentration. The dilution system described in Reference No. 2 was used.

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The three test levels were generated in two generation attempts. The 2X and 1X levels were generated in the first generation, and the 0.5X level was generated in the second generation.

Samples were collected for 60 minutes at approximately 1.5 liters per minute.

Collection Efficiency

Collection efficiency was determined at a concentration of 2.60 mg/cu m by connecting a filter in series to a backup filter and to a backup bubbler containing 15 ml of iso-octane. Samples were collected for 60 minutes at a flow rate of 1.5 liters per minute. The collection efficiency of the single filter was determined to be 1.00 since no DDT was detected in any of the backup filters or backup bubblers, at a detection limit of 0.05 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below:

mg/cu m found in the first filter	mg/cu m found backup filter	mg/cu m found backup bubbler	Collection Efficiency
2.575	N.D.*	N.D.*	1.00
2.713	"	"	"
2.676	"	"	"
2.474	"	"	"
2.617	"	"	"
2.542	"	"	"

*N.D. = Not detected at a detection limit of 0.05 mg/cu m.

Discussion

To test the possibility that DDT would not be totally collected as a particulate, the following experiment was performed. Three 37-mm Type AE glass fiber filters were spiked with 90 micrograms of DDT using 4-microliter aliquots of a solution of DDT in a benzene/iso-octane solution (1:5) containing 22.5 micrograms/microliter. Benzene was used to help dissolve the DDT quickly. This represents the amount of DDT that would be collected at 1X the OSHA standard in a 90-liter sample. The solvent was allowed to evaporate and 90 liters of air, at a flow rate of approximately 1.5 liters per minute was pulled through the filters. The filters were then analyzed to determine the amount of DDT recovered. The results of the experiment are presented below:

Micrograms Taken	Micrograms Found		Recovery
90.0	95.0		1.056
90.0	95.0		1.056
90.0	93.4		1.038
		mean	1.050
		std dev	0.010

From the above results, it was concluded that DDT would be collected efficiently using a single glass fiber filter.

A time study was conducted by spiking six glass fiber filters. The samples were stored for one week before analysis. The samples were extracted in 15 ml of iso-octane.

The time study was conducted at 1X the OSHA standard using 4 microliters of a stock solution of DDT in a benzene/iso-octane solution (1:5) containing 22.5 micrograms/microliter. The results given below were compared with the 1X data in the Analysis table which represents samples which were analyzed immediately.

Micrograms Taken	Micrograms Found		Recovery
90.0	91.6		1.018
90.0	87.4		0.971
90.0	86.8		0.964
90.0	86.2		0.958
90.0	87.3		0.970
90.0	87.5		0.972
		mean	0.976
		std dev	0.021

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.021$ $\overline{CV}_2 = 0.034$ $\overline{CV}_T = 0.061$

Data Sheet: DDT S274

Analysis

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
45.0	49.5	1.100	90.0	92.7	1.030	180.0	182.1	1.012
45.0	47.9	1.064	90.0	95.3	1.059	180.0	183.4	1.019
45.0	50.0	1.111	90.0	94.6	1.051	180.0	189.8	1.054
45.0	47.3	1.051	90.0	94.3	1.048	180.0	183.2	1.018
45.0	48.2	1.071	90.0	96.4	1.071	180.0	183.0	1.017
45.0	50.7	1.127	90.0	92.5	1.028	180.0	181.4	1.008
n=		6			6			6
mean		1.087			1.048			1.021
std dev		0.030			0.017			0.017
CV_1		0.028			0.016			0.017

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{AMR}}$ 0.023

The average Analytical Method Recovery (A.M.R.) at each level was used to calculate the corresponding corr. µg at each level in the Sampling and Analysis table.

Data Sheet: DDT S274

Sampling and Analysis

Test Level	Found			
	µg	Corr. µg	Liters	mg/cu m*
0.5S	46.3	42.6	85.2	0.500
	47.5	43.7	87.6	0.499
	43.6	40.1	85.2	0.471
	46.7	43.0	87.6	0.491
	43.2	39.7	80.4	0.494
	47.8	44.0	86.4	0.509
			n = 6	
			mean	0.494
			std dev	0.013
			CV_2	0.026
	119.1	113.6	80.4	1.413
	116.0	110.7	85.8	1.290
	122.7	117.1	86.4	1.355
	128.4	122.5	86.4	1.418
	130.3	124.3	86.4	1.439
	121.3	115.7	84.6	1.368
			n = 6	
			mean	1.381
			std dev	0.055
			CV_2	0.040
	238.2	233.3	90.6	2.575
	249.3	244.2	90.0	2.713
	234.4	229.6	85.8	2.676
	213.7	209.3	84.6	2.474
	235.6	230.8	88.2	2.617
	233.6	228.8	90.0	2.542
			n = 6	
			mean	2.600
			std dev	0.088
$\overline{CV}_2$ 0.034			CV_2	0.034

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: Aldrin, No. S275

OSHA Standard: 0.25 mg/cu m - skin

Chemicals Used Aldrite, emulsifyable concentrate (for generation of test atmospheres

Aldrin, reagent grade (for analytical validation)

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S275. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 180-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of a 112.75 mg/10 ml solution of aldrin in a benzene-iso-octane solution (1:5) were spiked onto 37-mm glass fiber filters. The analyte was extracted from the filters with 15 ml of iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S275.

Test atmospheres of aldrin at concentrations of approximately 0.5X, 1X, and 2X the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type A glass fiber filters connected in series with a midget bubbler containing 15 ml of iso-octane.

Generation

Samples of aldrin in air were generated by the procedure described in Reference No. 1. However, the system was modified by installing a secondary cyclone to further maintain the proper particle size distribution. Two additional modifications were necessary to generate the required levels of aldrin.

1. An air sleeve was installed at the entrance of the primary cyclone.

2. A tee was installed prior to entry into the dilution system allowing a measured quantity of concentrated vapors to be drawn off.

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These modifications were necessary to generate the proper concentration levels of aldrin in the generator system. A 0.25% solution of aldrin in toluene (15.6 ml of aldrite, which contains 64% of aldrin, made up to a 1-liter volume with toluene) was used in the aspiration system for the generation of aldrin.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples collected for at least ten minutes, and these samples analyzed. The results of the analyses were used to select conditions to reach the required concentration. The three stage dilution system described in Reference No. 2 was used. The three test levels were generated in two generation attempts. The 2X and 1X levels were generated in one generation, and the 0.5X level was generated in the second generation.

Samples were collected for 180 minutes at approximately 0.9 liter/min.

Collection Efficiency

Collection efficiency was determined at a concentration of 8.42 mg/cu m by connecting a filter and two midget bubblers (each containing 15 ml of iso-octane) in series. Samples were collected for 180 minutes at a flow rate of 0.9 liter per minute. The collection efficiency of the single filter and bubbler was determined to be 1.00 since no aldrin was detected in any of the second bubblers at a detection limit of 0.017 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below.

Total Concentration Found in the Filter and First Bubbler	Concentration Found in the Second Bubbler	Collection Efficiency
6.87 mg/cu m	N.D.*	1.00
9.83 "	"	"
9.17 "	"	"
7.47 "	"	"
8.75 "	"	"

*N.D. = Not detected at a detection limit of 0.017 mg/cu m.

Discussion

To test the possibility that aldrin would not be totally collected as a particulate on a filter, the following experiment was performed. Three 37-mm Type A glass fiber filters were spiked with 45.1 micrograms of aldrin using 4-microliter aliquots of a solution of aldrin in a benzene/iso-octane solution (1:5) containing 11.275 mg/ml. Benzene was used to help dissolve the aldrin quickly. This represents the amount of aldrin that would be collected at the 1X OSHA standard level in a 180-liter sample. The solvent was allowed to evaporate and 200 liters of air, at a flow rate of approximately 1.0 liter per minute, was pulled through the filters. The filters were then analyzed to determine the amount of aldrin recovered. The results of the experiment are presented on the next page.

Micrograms Taken	Micrograms Found	Recovery (%)
45.1	26.1	57.9
45.1	20.1	44.6
45.1	21.6	47.9
	mean	50.1

From the above results, it was demonstrated that filter collection is inadequate, because some of the material was volatilized off the filter. The material which vaporized off the filter would have to be collected on either a solid sorbent (i.e. charcoal) or in an organic solvent (in a midget bubbler).

Since aldrin was generated from an organic solvent, the high concentrations of organic solvent vapor could prevent efficient collection of the aldrin vapor on charcoal. The collection efficiency tests showed that aldrin is collected efficiently using a filter-bubbler assembly.

A time study was conducted by spiking six glass fiber filters and extracting them immediately in 15 ml of iso-octane. The samples were stored for one week before analysis. The time study was conducted at 1X the OSHA standard level using 4 microliters of a stock solution of aldrin in a benzene/iso-octane solution (1:5) containing 112.75 mg/10 ml. The results given below were compared with the 1X data in the Analysis table which represents samples which were analyzed immediately.

mg taken	mg found	Recovery $(\frac{\text{Found}}{\text{Taken}})$
0.0450	0.0467	1.038
0.0450	0.0468	1.040
0.0450	0.0460	1.022
0.0450	0.0463	1.029
0.0450	0.0478	1.062
0.0450	0.0448	0.996
	mean	1.031
	std dev	0.022

It was concluded that aldrin is stable for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.012$ $\overline{CV}_2 = 0.077$ $\overline{CV}_T = 0.092$

Data Sheet: Aldrin S275

Analysis

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
22.55	23.00	1.020	45.1	44.5	0.987	90.2	90.4	1.002
22.55	23.20	1.029	45.1	45.5	1.009	90.2	90.3	1.001
22.55	22.70	1.007	45.1	44.5	0.987	90.2	88.2	0.978
22.55	22.56	1.000	45.1	45.2	1.002	90.2	89.9	0.997
22.55	23.13	1.026	45.1	45.2	1.002	90.2	90.4	1.002
22.55	22.26	0.987	45.1	44.4	0.984	90.2	89.4	0.991
n=		6			6			6
mean		1.012			0.995			0.995
std dev		0.016			0.010			0.009
CV_1		0.016			0.010			0.009

$\overline{CV_1}$ 0.012

$\overline{CV_{A+\overline{AMR}}}$ 0.013

Based on the above results, no correction for Analytical Method Recovery (A.M.R.) is necessary.

Data Sheet: Aldrin S275

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	19.7	153	0.129
	25.0	162	0.154
	27.5	169	0.163
	25.2	176	0.143
	25.4	161	0.158
	24.7	168	0.147
		n=6	
		mean	0.149
		std dev	0.012
		CV_2	0.081
1S	38.2	161	0.237
	35.8	165	0.217
	40.4	160	0.252
	38.7	160	0.242
	45.1	175	0.258
	36.4	170	0.214
		n=6	
		mean	0.237
		std dev	0.018
		CV_2	0.076
2S	80.2	170	0.472
	87.1	160	0.544
	86.3	161	0.536
	76.7	160	0.479
	79.8	165	0.484
	79.7	175	0.455
		n=6	
		mean	0.495
		std dev	0.036
		CV_2	0.073

$\overline{CV_2}$ 0.077

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: p-Dichlorobenzene, No. S281

OSHA Standard: 75 ppm (450 mg/cu m)

Chemical Used for Validation: p-Dichlorobenzene
Aldrich

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of p-dichlorobenzene in air is described in NIOSH Method S281, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of p-dichlorobenzene to represent 3-liter air samples. Laboratory generated samples of p-dichlorobenzene in air were collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The analyte was desorbed with carbon disulfide. Analysis was by gas chromatography using an automatic sample injector. The results were corrected for desorption efficiency. The "found" concentrations of p-dichlorobenzene in air were determined by dividing the corrected mg found by the volume sampled (critical orifice flow rate for that sample X 68.8 minutes). It was not possible to determine the "true" concentration in the generation system. However, it was possible to monitor the stability of the 2X concentration level using a total hydrocarbon analyzer. Collection efficiency was determined by analyzing the backup sections of the charcoal tubes. Collection efficiency was determined to be 1.00 at a detection limit of 30 mg/cu m.

Modification

One major modification of P&CAM 127 was made. An acetone solution of p-dichlorobenzene (338.2 micrograms/microliter) was used to apply the analyte to the charcoal, because p-dichlorobenzene is a solid. Hexane and methanol were tried as possible solvents, but were unsatisfactory due to low solubility of p-dichlorobenzene.

Generation

Samples of p-dichlorobenzene were generated by the procedure described in Reference No. 1 using the two-piece vapor generator. The generator conditions used are given on the next page.

Nitrogen flow rate:	186 ml/min at 23°C
Dilution air flow rate:	8.75 liters/min - primary dilution at 23°C
	38.7 liters/min - secondary dilution at 23°C

Oil bath at 75°C

The approximate concentration of p-dichlorobenzene that was desired in the sampling chamber was obtained as follows. The total hydrocarbon analyzer was calibrated with a chlorobenzene bag standard, at a concentration of 680 mg/cu m (6.10 millimoles/cu m). (The 2X level of p-dichlorobenzene is equivalent to 6.10 millimoles/cu m). An estimate was made of the hydrocarbon analyzer response for p-dichlorobenzene at 2X the standard, using the results of the chlorobenzene bag standard as a guide. Flow rates of dilution gases through the generator were adjusted until the concentration in the sampling chamber was approximately at the desired level. Chlorobenzene was used to calibrate the hydrocarbon analyzer, because it was expected to give a similar response to p-dichlorobenzene on the hydrocarbon analyzer, and because it is a liquid so bag standards can be easily prepared.

Later, a test was conducted to determine the relative response of the flame ionization detector of a gas chromatograph to chlorobenzene and p-dichlorobenzene. Equimolar solutions of the two compounds were gas chromatographed, and the peak areas measured by a Spectra Physics IV integrator. The resulting areas were in the ratio

$$\frac{\text{chlorobenzene}}{\text{p-dichlorobenzene}} = 1.02$$

Using this result, and the relative response of the hydrocarbon analyzer to the bag standard and the 2X chamber, it was calculated that the concentration of p-dichlorobenzene in the 2X chamber during sample collection was 831 mg/cu m.

The concentration in this chamber as determined by the mean of the results for analyses of the six samples (p. S281-5) was 777 mg/cu m. These two results are within 6.5% of one another.

In addition to this calibration test, the following tests were done to assess whether the concentration "found" at each level was an unbiased measure of the concentration in the air sampled:

1. Breakthrough test (see below) indicated that the capacity of the charcoal for this analyte was sufficient.

2. Collection efficiency was determined to be 1.00. This is based on examination of the backup section from each of the six samples at the 2X level.

Based on these tests, the "found" and "taken" concentrations were considered to be equal.

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test. Less than 5% of the generated concentration of 777 mg/cu m (as determined by analysis of samples taken at the 2X level) in the effluent was observed after 240 minutes of sampling at a rate of 0.045 liter per minute at which time the test was discontinued. Breakthrough was not observed.

Collection Efficiency

Collection efficiency tests were conducted at a concentration of 777 mg/cu m by analyzing the backup sections of the charcoal tubes. Collection efficiency was determined to be 1.00, since no p-dichlorobenzene was detected at a detection limit of 30 mg/cu m. The results are given below:

mg/cu m found front section	mg/cu m found backup section	Collection Efficiency
781	N.D. *	1.00
760	N.D.	1.00
775	N.D.	1.00
779	N.D.	1.00
779	N.D.	1.00
789	N.D.	1.00

* N.D. = Not detected at a detection limit of 30 mg/cu m.

Precision

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.022$ $\overline{CV}_2 = 0.011$ $\overline{CV}_T = 0.052$

Data Sheet: p-Dichlorobenzene S281

Analysis

Level	0.5X			1X			2X	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.676	0.622	0.920	1.353	1.195	0.883	2.706	2.447	0.904
0.676	0.602	0.891	1.353	1.224	0.905	2.706	2.500	0.924
0.676	0.579	0.857	1.353	1.207	0.892	2.706	2.463	0.910
0.676	0.630	0.932	1.353	1.236	0.914	2.706	2.507	0.926
0.676	0.624	0.923	1.353	1.205	0.891	2.706	2.475	0.915
0.676	0.627	0.928	1.353	1.246	0.921	2.706	2.515	0.929
n =		6			6			6
mean		0.908			0.901			0.918
std dev		0.029			0.015			0.010
CV_1		0.032			0.017			0.011

$\overline{CV}_1$ 0.022

$\overline{CV}_{A+\overline{DE}}$ 0.024

The equation D.E. = $0.911 - e^{-8.22 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: p-Dichlorobenzene S281

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.507	0.566	3.05	185.6
	0.520	0.580	3.13	185.3
	0.496	0.555	3.08	180.2
	0.492	0.551	3.03	181.8
	0.499	0.558	3.05	183.0
	Sample was lost.			
			n = 5	
			mean	183.2
			std dev	2.3
			CV_2	0.013
1S	1.083	1.189	3.18	374
	1.055	1.158	3.10	374
	1.091	1.198	3.18	377
	1.045	1.147	3.08	372
	1.061	1.165	3.08	378
	1.052	1.155	3.05	379
			n = 6	
			mean	376
			std dev	3
			CV_2	0.008
2S	2.143	2.352	3.01	781
	2.145	2.355	3.10	760
	2.167	2.379	3.07	775
	2.165	2.376	3.05	779
	2.149	2.359	3.03	779
	2.258	2.479	3.14	789
			n = 6	
			mean	777
			std dev	10
$\overline{CV}_2$ 0.011			CV_2	0.013

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: Dieldrin, No. S283

OSHA Standard: 0.25 mg/cu m - skin

Chemical Used for Validation: Dieldrin, analytical reagent (for analytical method validation) Applied Science Laboratory, Inc.

Commercial Dieldrin, Namco (for generation of test atmospheres)

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S283. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 180-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of a 11.25 micrograms/microliter solution of dieldrin in a benzene/iso-octane solution (1:5) were spiked onto 37-mm glass fiber filters. The analyte was extracted from the filters with 15 ml of iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S283.

Test atmospheres of dieldrin at concentrations of approximately 0.5X, 1X, and 2X the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type AE glass fiber filters.

Generation

Samples of dieldrin in air were generated by the procedure described in Reference No. 1. However, the system was modified by installing a secondary cyclone to further maintain the proper particle size distribution. A tee was installed prior to the entry of the mixing chamber allowing a measured quantity of air laden with dieldrin to be drawn off and discarded in order to decrease the amount of dieldrin entering the mixing chamber. A 0.5% solution of dieldrin in toluene (25 ml dieldrin made up to 1 liter with toluene) was used for the generation of test atmospheres of dieldrin.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples collected for at least ten minutes, and these samples analyzed. The results of the analyses were used to select conditions to reach the required concentration. The dilution system described in Reference No. 2 was used.

The three test levels were generated in two generation attempts. The 2X and 1X levels were generated in the first generation, and the 0.5X level was generated in the second generation.

Samples were collected for 120 minutes at approximately 1.5 liters per minute.

Collection Efficiency

Collection efficiency was determined at a concentration of 0.587 mg/cu m by connecting a filter in series to a backup filter and to a backup bubbler containing 15 ml of iso-octane. Samples were collected for 120 minutes at a flow rate of 1.5 liters per minute. The collection efficiency of the single filter was determined to be 1.00 since no dieldrin was detected in any of the backup filters or backup bubblers at a detection limit of 0.06 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below:

	mg/cu m found in the first filter	mg/cu m found backup filter	mg/cu m found backup bubbler	Collection Efficiency
	0.582	N.D.*	N.D.*	1.00
	0.590	"	"	"
	0.627	"	"	"
	0.585	"	"	"
	0.560	"	"	"
	0.576	"	"	"
mean	0.587			

*N.D. = Not detected at a detection limit of 0.06 mg/cu m.

Discussion

To test the possibility that dieldrin would not be totally collected as a particulate, the following experiment was performed. Three 37-mm Type AE glass fiber filters were spiked with 44.9 micrograms of dieldrin using 4-microliter aliquots of a solution of dieldrin in a benzene/iso-octan solution (1:5) containing 11.25 micrograms/microliter. Dieldrin is adequately soluble in iso-octane for sampling and analysis of air samples. However, the rate of solution in iso-octane is slow, so benzene was used in this portion of the study to help dissolve the dieldrin quickly. This represents the amount of dieldrin that would be collected at 1X the OSHA standard in a 180-liter sample. The solvent was allowed to evaporate and 180 liters of air, at a flow rate of approximately 1.5 liters per minute was pulled through the filters. The filters were then analyzed to determine the amount of dieldrin recovered. The results of the experiment are presented below:

micrograms taken	micrograms found		Recovery
44.9	44.6		0.993
44.9	44.1		0.982
44.9	44.6		0.993
		mean	0.989
		std dev	0.006

From the above results, it was concluded that dieldrin would be collected efficiently using a single glass fiber filter.

A time study was conducted by spiking six glass fiber filters. The samples were stored for one week before analysis. The samples were extracted in 15 ml of iso-octane.

The time study was conducted at 1X the OSHA standard using 4 microliters of a stock solution of dieldrin in a benzene/iso-octane solution (1:5) containing 11.25 micrograms/microliter. The results given below were compared with the 1X data in the Analysis table which represents samples which were analyzed immediately.

micrograms taken	micrograms found		Recovery
44.9	44.5		0.991
44.9	44.7		0.996
44.9	44.9		1.000
44.9	44.8		0.998
44.9	43.8		0.976
44.9	44.6		0.993
		mean	0.992
		std dev	0.009

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.013$ $\overline{CV}_2 = 0.070$ $\overline{CV}_T = 0.086$

Data Sheet: Dieldrin S283

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
22.47	22.61	1.006	44.9	45.4	1.011	89.9	91.9	1.022
22.47	23.04	1.025	44.9	45.3	1.009	Sample was lost		
22.47	23.40	1.041	44.9	46.0	1.024	89.9	92.7	1.031
22.47	22.80	1.015	44.9	44.9	1.000	89.9	95.1	1.058
22.47	23.00	1.024	44.9	45.9	1.022	89.9	93.0	1.034
22.47	22.94	1.021	44.9	44.4	0.989	89.9	93.4	1.039

n =	6	6	5
mean	1.022	1.009	1.037
std dev	0.012	0.013	0.013
CV_1	0.012	0.013	0.013

$\overline{CV}_1$ 0.013

$\overline{CV}_{A+\overline{AMR}}$ 0.014

Data Sheet: Dieldrin S283

Sampling and Analysis

Test Level		Found		
		µg	Liters	mg/cu m*
0.5S		19.28	174.2	0.111
		20.29	176.6	0.115
		20.86	181.5	0.115
		21.95	176.6	0.124
		21.10	165.6	0.127
		21.59	154.7	0.140
			n = 6	
			mean	0.122
			std dev	0.011
			CV_2	0.090
1S		36.8	165.6	0.222
		38.9	170.4	0.228
		38.2	176.4	0.217
		43.8	174.0	0.252
		38.3	170.4	0.225
		34.6	171.4	0.202
			n = 6	
			mean	0.224
			std dev	0.016
			CV_2	0.071
2S		95.0	163.2	0.582
		102.0	172.8	0.590
		103.4	165.0	0.627
		91.2	156.0	0.585
		100.6	179.8	0.560
		101.0	175.2	0.576
			n = 6	
			mean	0.587
			std dev	0.022
$\overline{CV_2}$	0.070		CV_2	0.037

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

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References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	EPN (O-Ethyl-O-p-nitrophenyl phenylphosphonothioate) No. S285
OSHA Standard:	0.5 mg/cu m - skin
Chemicals Used for Validation:	Trion-6 (for generating test atmospheres of EPN) Wilbur Ellis Company
	EPN, reagent grade (for analytical validation) Applied Science Labs

Procedure

The general procedure used is described in NIOSH Method No. S285. The analytical method was tested at concentrations equal to that present in a 120-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot (2, 4, and 8 microliters) of a 15 mg/ml solution of EPN in iso-octane was added to 37-mm Type A glass fiber filters. EPN was extracted from the filter with iso-octane and analyzed by gas chromatography using a flame photometric detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S285. Test atmospheres of EPN at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on glass fiber filters. The results of analysis of these samples are given in the Sampling and Analysis table. The average size of the particles was approximately one micron diameter.

Generation

Samples of EPN in air were generated by the procedure described in Reference No. 1. However, the aspirator output was divided by means of a splitter prior to entry into the dilution system. This was necessary to generate the desired concentration levels in the generator system.

A 0.5% solution of EPN in toluene (20 ml of Trion-6 which contains 25% of EPN made up to a 1-liter volume with toluene) was used in the aspiration system for the generation of EPN.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples were collected for at least ten minutes, and these samples were analyzed. These results were used to select conditions to reach the desired concentration. When the desired concentration was reached, six samples at each of the three levels were collected simultaneously using the three stage dilution system described in Reference No. 2. Samples were collected for 80 minutes at approximately 1.5 liter/minute.

Collection Efficiency

Collection efficiency tests were conducted at 1.156 mg/cu m (as determined by analysis of samples collected at 2X the OSHA standard level) by mounting in series two filters in direct contact with each other followed by a midget bubbler containing 15 ml of iso-octane. The results of the collection efficiency test are given below:

mg/cu m found first filter	mg/cu m found backup filter	mg/cu m found backup bubbler	Collection Efficiency
1.159	N.D. *	N.D. *	1.00
1.170	"	"	1.00
1.172	"	"	1.00
1.179	"	"	1.00
1.131	"	"	1.00
1.128	"	"	1.00

*N.D. = not detected at a detection limit of 1.74×10^{-5} mg/cu m

Since collection efficiency was determined to be 1.00, no correction for collection efficiency is needed in this method.

Discussion

The following experiment was conducted to ascertain whether filter collection would be appropriate for the collection of EPN. Two filters were spotted with 4 µl of a stock solution of EPN in iso-octane containing 15 mg/ml. After spiking, each filter was placed in a filter cassette. Each filter was connected in series to a midget bubbler containing 15 ml of iso-octane. Air was pulled through the two filter-bubbler combination at a flow rate of 1 liter per minute for two hours. The filter and bubbler were then analyzed for EPN. It was found that EPN remained on the filter. No EPN was detected in the bubbler. It was concluded that the analyte would be present as a particulate and it would not be vaporized from the filter after collection. Filter collection was therefore selected. During sample collection a backup support pad was not needed in holding the filter in place, but it was recommended that one be used.

A time study was conducted by spiking six glass fiber filters and allowing them to stand for one week in closed containers before analysis. The samples were exposed to light during storage. The time study was conducted at 1X the OSHA standard level using 4 µl of a stock solution of EPN in iso-octane (15 mg/ml). The filters were extracted with 15 ml of iso-octane and analyzed by GC equipped with a flame photometric detector. The results given below were compared with the 1X data in the Analysis table which represents samples which were analyzed immediately.

mg taken	mg found	Recovery
0.0600	0.0569	0.948
0.0600	0.0576	0.960
0.0600	0.0565	0.942
0.0600	0.0575	0.958
0.0600	0.0577	0.962
0.0600	0.0567	0.945
	mean	0.952
	std dev	0.009

From the above results, EPN is adequately stable on glass fiber filters for at least one week.

Precision and Accuracy

The statistical procedures are described in Reference No. 3.

$\overline{CV}_1 = 0.037$ $\overline{CV}_2 = 0.028$ $\overline{CV}_T = 0.059$

Data Sheet: EPN S285

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.0300	0.0315	1.050	0.0600	0.0619	1.032	0.1200	0.1206	1.005
0.0300	0.0306	1.020	0.0600	0.0603	1.005	0.1200	0.1207	1.006
0.0300	0.0295	0.983	0.0600	0.0585	0.975	0.1200	0.1208	1.007
0.0300	0.0298	0.993	0.0600	0.0588	0.980	0.1200	0.1212	1.010
0.0300	0.0299	0.997	0.0600	0.0620	1.033	0.1200	0.1196	0.997
0.0300	0.0313	1.043	0.0600	0.0528	0.880	0.1200	0.1221	1.018
n =		6			6			6
mean		1.014			0.984			1.007
std dev		0.028			0.057			0.007
CV_1		0.028			0.058			0.007

$\overline{CV}_1$ 0.037

$\overline{CV}_{A+\overline{AMR}}$ 0.040

Data Sheet: EPN S285

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.0324	110.4	0.2935
	0.0300	109.6	0.2737
	0.0349	114.4	0.3051
	0.0352	116.4	0.3024
	0.0349	117.2	0.2978
	0.0347	117.2	0.2961
		n = 6	
		mean	0.2948
		std dev	0.0111
		CV_2	0.038
1S	0.0804	115.2	0.698
	0.0740	113.2	0.654
	0.0752	113.6	0.662
	0.0744	110.4	0.674
	0.0729	108.0	0.675
	0.0772	116.0	0.666
		n = 6	
		mean	0.672
		std dev	0.015
		CV_2	0.022
2S	0.1414	122.0	1.159
	0.1418	121.2	1.170
	0.1406	120.0	1.172
	0.1349	114.4	1.179
	0.1375	121.6	1.131
	0.1282	113.6	1.128
		n = 6	
		mean	1.156
		std dev	0.022
$\overline{CV}_2$ 0.028		CV_2	0.019

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Ethylene Oxide, No. S286

OSHA Standard: 50 ppm (90 mg/cu m)

Chemical Used for Validation: Ethylene Oxide, Matheson Gas Products, 99.7%
Ethylene Oxide, Fisher Scientific Co., highest purity, b.p. 10.5-11.5°C

Procedure

The general procedure used is described in NIOSH Method No. S286 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate aliquot of a solution of ethylene oxide in carbon disulfide represented in a 5-liter air sample. The charcoal used was Lot 105 coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in 5-ml tubes with Teflon-lined screw caps. Alternatively, the 5-ml vials with Teflon-lined screw caps distributed by SKC, Inc., were also used. Sample vials or tubes were capped tightly immediately after the addition of carbon disulfide to minimize loss of ethylene oxide during the desorption process. After the 30-minute desorption period, a portion of the carbon disulfide extracts was transferred to the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve derived from the data shown in Table 1. Details of the analysis procedure may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 has been modified as follows: The sampling tube series recommended consists of two separate tubes--a front adsorbing tube containing 400 mg of charcoal (prepared from a regular commercially available large tube by removing the backup section) and connected in series with a short piece of tubing to a second tube containing 200 mg of charcoal (similarly prepared from a regular large tube by removing the front section). The charcoal from each front and backup tube is desorbed with 2 ml of carbon disulfide; this volume is adequate for the 400 mg and 200 mg batches of charcoal.

Discussion

Lot 105 activated coconut charcoal was used for all studies with ethylene oxide. The large charcoal tubes are recommended because the small tubes do not have sufficient capacity for ethylene oxide so as to satisfy minimum sampling time requirements.

TABLE 1

Data Sheet: Ethylene Oxide, S286
(Lot 105 charcoal/400 mg; Samples Stored 1 Day)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
252.7	180.3	0.713	505	391	0.774	1011	836	0.827
252.7	186.7	0.739	505	419	0.830	1011	802	0.793
252.7	179.2	0.709	505	406	0.804	1011	825	0.816
252.7	192.4	0.761	505	396	0.784	1011	829	0.820
252.7	194.5	0.770	505	393	0.778	1011	807	0.798
252.7	188.3	0.745	505	409	0.810	1011	793	0.784
n =		6			6			6
mean		0.740			0.797			0.806
std dev		0.0247			0.0218			0.0170
CV_1		0.0334			0.0273			0.0212

$\overline{CV}_1$ 0.0278

$\overline{CV}_{A+\overline{DE}}$ 0.0300

Ethylene oxide from two sources was used for these validation studies. Handling of liquid ethylene oxide proved to be troublesome because of its low boiling point (10.5°C-11.5°C) and thus ethylene oxide in a gas cylinder was subsequently used for all studies.

A stock solution of ethylene oxide was prepared by bubbling ethylene oxide gas in carbon disulfide and allowing the solution to equilibrate at room temperature for two hours prior to determining the ethylene oxide concentration by comparison with a gas standard mixture of ethylene oxide in air. (The gas standard was prepared by adding a known volume of ethylene oxide gas into an evacuated gas bulb and equilibrating with air at atmospheric temperature and pressure.) The stock solution of ethylene oxide in carbon disulfide was used for the preparation of the spiked analytical samples and also for the preparation of the calibration standards used for the various analyses over the 12-day period in which these experimental studies were conducted. The stock solution was stored in the refrigerator and was assayed at various intervals during this period. The data obtained from the independent studies summarized below show that the stock solution is stable for at least 7 days. The average concentration found was 36.1 µg/µl with a coefficient of variation of 8%. This average concentration was used for all calculations. Unfortunately, no independent calibration of this stock solution was carried out on the last day this solution was used.

Date	Found Concentration in µg/µl
6/3/76	33.1
6/7/76	38.7
6/10/76	36.5
6/14/76	Not analyzed

The GC analysis of all samples was done on a 6'x1/8" stainless steel column packed with Porapak QS, 100/120 mesh. The analyses were carried out using the external standard method because no suitable internal standard (i.e., a component with a retention time close to that of the analyte and which is not adsorbed by charcoal) was found. However, standard solutions of methanol in carbon disulfide were also analyzed in order to tab the accuracy of the gas calibration standard (i.e., the GC response constant in Area per µg for ethylene oxide is approximately equivalent to that of methanol).

Stability studies were done using two sets of generated samples. The first set of 18 samples (refer to Table 2) was stored at room temperature for 6 days while the second set was handled such that 9 samples, 3 at each of the 3 test levels, were analyzed after one day while the rest were stored at room temperature for six days (refer to Table 3). The data in Table 2 show an average recovery of 93% for the 18 samples stored for six days while the data in Table 3 show a recovery of 96% for the 1-day-old samples and 109% for the 6-day-old samples. The higher value obtained for the six-day-old

TABLE 2

Data Sheet: Ethylene Oxide, S286
(Lot 105 charcoal/400 mg; Samples Stored 6 Days)

Sampling and Analysis

Test Level	Found				Taken	
	µg	Corr µgΔ	Liters	mg/cu m	mg/cu m	Recovery
0.5S	280.5	344	4.94	69.7	62.9	
	240.6	299	4.87	61.4	62.9	
	240.7	299	5.14	58.2	62.9	
	235.3	292	5.29	55.2	62.9	
	239.8	298	5.32	56.0	62.9	
	219.3	274	5.21	52.6	62.9	
			n = 6			
			mean	58.9		
			std dev	6.09		0.936
			CV_2	0.1034		
1S	488	610	5.01	121.8	131	
	438	551	4.94	111.5	131	
	502	628	4.94	127.1	131	
	473	591	4.81	122.9	131	
	456	574	4.87	117.9	131	
	449	565	4.87	116.0	131	
			n = 6			
			mean	119.5		0.912
			std dev	5.54		
			CV_2	0.0464		
2S	1014	1237	4.81	257.2	270	
	1040	1268	4.87	260.4	270	
	993	1211	4.94	245.1	270	
	1010	1232	5.21	236.5	270	
	995	1213	4.81	252.2	270	
	1021	1245	4.87	255.6	270	
			n = 6			
			mean	251.1		0.930
			std dev	8.88		
			CV_2	0.0354		
			$\overline{CV}_2$	0.0686		

ΔCorrected for DE factor

TABLE 3

Stability of Ethylene Oxide on Lot 105 Charcoal

Test Level	Samples Stored 1 Day			Samples Stored 6 Days**		
	µg	Found Liters	mg/cu m	µg	Found Liters	mg/cu m
0.5S	242.7	4.94	49.1	274.8	5.34	51.5
	257.3	4.92	52.3	317.0	5.38	58.9
	243.8	5.19	47.0	254.6	5.26	48.4
	Mean		49.5			52.9
	CV		0.0539			0.102
	RecoveryΔ		98.7%			104.8%
1S	563	5.05	111.5	607	4.85	125.2
	458	4.94	92.7	609	4.92	123.8
	550	4.94	111.3	592	4.92	120.3
	Mean		105.2			123.1
	CV		0.103			0.0205
	RecoveryΔ		94.7%			110.0%
2S	1061	4.85	218.8	32*	5.26	6.1*
	1051	4.92	213.6	1268	4.85	261.4
	1104	4.94	223.5	1293	4.92	262.8
	Mean		218.6			262.1
	CV		0.0227			0.0038
	RecoveryΔ		93.5%			112.0%

ΔRecovery was calculated using the mg/cu m "found" corrected for the appropriate DE factor and the mg/cu m "taken" based on the total hydrocarbon calibration of the generator.

*Value excluded from statistical calculations.

**These samples were analyzed on 6/14/76.

samples could be due to uncertainties in the absolute concentration of the stock solution of ethylene oxide particularly because the concentration of this stock solution was not checked independently at that time span.

Generation

Test atmosphere samples were generated by delivering ethylene oxide gas from a cylinder via an orifice and needle valve to a dry air stream flowing at a rate of 0.100 cu m/min. The generator concentration was determined based on a calibration curve prepared by charging M^3 with known amounts of ethylene oxide gas and measuring the hydrocarbon response using a total hydrocarbon analyzer. The details of this calibration procedure are described in the Propane S87 Backup Data Report. The dilution ratios were maintained at 0.233, 0.486 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels.

Three sets of 18 generated samples were collected and analyzed as shown in Tables 2, 3 and 4. In the case of the first two sets of samples, the generator concentration was initially estimated based on the gas flow rate determined by using a calibrated rotameter. It was subsequently determined that the calculated generator concentration based on the flow rate does not agree with the data obtained using the total hydrocarbon analyzer; the generator concentratio based on THC calibration data is equal to 1.59 X flow rate data. This correction factor was applied in order to determine the generator concentration reported in Table 2 (63, 131, 270 mg/cu m) and Table 3 (66, 139, 285 mg/cu m). A third set of ethylene oxide samples was collected in order to cover the requisite concentration interval (41, 86 and 176 mg/cu m).

Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 2.1 mg of ethylene oxide when a test atmosphere containing 280 mg/cu m of ethylene oxide in air was sampled at 0.19 liter per minute for 40 minutes; at that time the concentration of analyte in the effluent was 5% of that in the influent.

In addition, the backup sections of the 5-liter samples collected at 0.06 liter per minute at 2X the OSHA standard level were also analyzed. No ethylene oxide was found in any of the three sets of six backup tubes analyzed.

Precision and Accuracy

The statistical procedures used are described in Reference 1; the statistical calculations were done using the data in Tables 1 and 4.

TABLE 4

Data Sheet: Ethylene Oxide, S286
(Lot 105 charcoal/400 mg; Sample stored 1 day)

Sampling and Analysis

Test Level	Found				Taken	
	µg	Corr µgΔ	Liters	mg/cu m	mg/cu m	Recovery
0.5S	162.1	223.6	4.99	44.8	41.0	
	153.9	212.3	4.93	43.1	41.0	
	178.1	242.3	5.20	46.6	41.0	
	120.9	170.3	5.35	31.8	41.0	
	153.0	212.5	5.38	39.5	41.0	
	162.5	224.1	5.27	42.5	41.0	
			n = 6			
			mean	41.4		1.010
			std dev	5.26		
			CV_2	0.1271		
1S	329	425	5.06	84.0	85.5	
	331	424	4.99	85.0	85.5	
	341	437	4.99	87.6	85.5	
	316	408	4.86	84.0	85.5	
	333	427	4.93	86.6	85.5	
	307	399	4.93	80.9	85.5	
			n = 6			
			mean	84.7		0.991
			std dev	2.346		
			CV_2	0.0277		
2S	528	656	4.86	135.0	175.9	
	664	820	4.93	166.3	175.9	
	630	778	4.99	155.9	175.9	
	707	867	5.27	164.5	175.9	
	653	806	4.86	165.8	175.9	
	689	851	4.93	172.6	175.9	
			n = 6			
			mean	160.0		0.910
			std dev	13.37		
			$\frac{CV_2}{CV_2}$	0.0836 / 0.0893		

ΔCorrected for DE factor

$\overline{CV}_1 = 0.0278$ $\overline{CV}_2 = 0.0893$ $\overline{CV}_T = 0.103$

The average recovery of the generated samples over all levels was 97%.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Backup Data Report

Substance:	Lindane, No. S290
OSHA Standard:	0.5 mg/cu m - skin
Chemicals Used for Validation:	ortho-Lindane, Borer and Leaf Miner Spray (for generation of test atmospheres)
	Lindane, reagent grade (for analytical validation)

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method No. S290. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 90-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of a 11.25 mg/ml solution of lindane in a benzene-iso-octane solution (1:5) were spiked onto 37-mm glass fiber filters. The analyte was extracted from the filters with 15 ml of iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S290.

Test atmospheres of lindane at concentrations of approximately 0.5X, 1X, and 2X the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on Type A glass fiber filters connected in series with a midget bubbler containing 15 ml of iso-octane.

Generation

Samples of lindane in air were generated by the procedure described in Reference No. 1. However, the system was modified by installing a secondary cyclone to further maintain the proper particle size distribution. A 1.5% solution of lindane in toluene (5 ml of commercial lindane containing 20% lindane, made up to a 1-liter volume with toluene)was used in the aspiration system for the generation of lindane.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples collected for at least ten minutes, and these samples analyzed. The results of the analyses were used to select conditions to reach the required concentration. The three stage dilution system described in Reference No. 2 was used.

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The three test levels were generated in two generation attempts. The 2X and 1X levels were generated in the first generation, and the 0.5X level was generated in the second generation.

Samples were collected for 60 minutes at approximately 1.5 liters/min.

Collection Efficiency

Collection efficiency was determined at a concentration of 2.22 mg/cu m by connecting a filter and two midget bubblers (each containing 15 ml of iso-octane) in series. Samples were collected for 60 minutes at a flow rate of 1.5 liters per minute. The collection efficiency of the single filter and bubbler was determined to be 1.00 since no lindane was detected in any of the second bubblers at a detection limit of 0.01 mg/cu m. Thus, no correction for collection efficiency is necessary. The results of the collection efficiency test are presented below.

Total Concentration Found in the Filter and First Bubbler	Concentration Found in the Second Bubbler	Collection Efficiency
2.27 mg/cu m	N.D.*	1.00
2.30 "	"	"
2.22 "	"	"
2.31 "	"	"
2.24 "	"	"
1.97 "	"	"

*N.D. = Not detected at a detection limit of 0.01 mg/cu m.

Discussion

To test the possibility that lindane would not be totally collected as a particulate on a filter, the following experiment was performed. Three 37-mm Type A glass fiber filters were spiked with 45.0 micrograms of lindane using 4-microliter aliquots of a solution of lindane in a benzene/iso-octane solution (1:5) containing 11.25 mg/ml. Benzene was used to help dissolve the lindane quickly. This represents the amount of lindane that would be collected at the 1X OSHA standard level in a 90-liter sample. The solvent was allowed to evaporate and 90 liters of air, at a flow rate of approximately 1.5 liters per minute, was pulled through the filters connected in series with midget bubblers containing 15 ml of iso-octane. The filters and bubblers were then analyzed separately to determine the amount of lindane recovered. The results of the experiment are presented below:

Micrograms Taken	Micrograms Found in Filter	Micrograms Found in in Backup Bubbler	Recovery
45.0	41.1	3.4	0.989
45.0	38.4	5.7	0.980
45.0	40.1	3.7	0.973
		mean	0.981

From the above results, it was concluded that it is necessary to use a filter-bubbler combination for the efficient collection of lindane.

A time study was conducted by spiking six glass fiber filters and extracting them immediately in 15 ml of iso-octane. The samples were stored for one week before analysis. The time study was conducted at 1X the OSHA standard level using 4 microliters of a stock solution of lindane in a benzene/iso-octane solution (1:5) containing 11.25 mg/ml. The results given below were compared with the 1X data in the Analysis table which represents samples which were analyzed immediately.

mg taken	mg found		Recovery
0.045	0.046		1.022
0.045	0.045		1.000
0.045	0.045		1.000
0.045	0.047		1.044
0.045	0.045		1.000
0.045	0.047		1.044
		mean	1.018
		std dev	0.022

It was concluded that lindane is stable in iso-octane solution for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.013$ $\overline{CV}_2 = 0.070$ $\overline{CV}_T = 0.086$

Data Sheet: Lindane S290

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
22.52	22.70	1.008	45.0	45.2	1.004	90.1	89.9	0.998
22.52	23.48	1.043	45.0	44.8	0.996	90.1	89.4	0.992
22.52	22.51	1.000	45.0	45.1	1.002	90.1	90.6	1.006
22.52	23.00	1.021	45.0	45.1	1.002	90.1	89.8	0.997
22.52	22.74	1.010	45.0	44.5	0.989	90.1	89.8	0.997
22.52	23.81	1.057	45.0	45.2	1.004	90.1	89.8	0.997
n=		6			6			6
mean		1.023			1.000			0.998
std dev		0.022			0.006			0.005
CV_1		0.022			0.006			0.005

$\overline{CV_1}$ 0.013

$\overline{CV_{A+\overline{AMR}}}$ 0.014

Based on the above results, no correction for Analytical Method Recovery (AMR) is necessary.

Data Sheet: Lindane S290

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	25.80	86.4	0.299
	20.94	82.2	0.255
	23.49	87.0	0.270
	23.20	88.2	0.263
	24.57	87.0	0.282
	25.84	85.8	0.301
		n = 6	
		mean	0.278
		std dev	0.019
		CV_2	0.068
1S	66.5	86.4	0.770
	56.2	82.2	0.684
	61.3	87.0	0.705
	58.2	88.2	0.660
	66.7	87.0	0.767
	68.4	85.8	0.797
		n = 6	
		mean	0.730
		std dev	0.055
		CV_2	0.075
2S	135.7	86.4	1.571
	152.1	82.8	1.837
	138.0	84.6	1.631
	147.8	86.4	1.711
	134.1	79.2	1.693
	132.0	86.4	1.528
		n = 6	
		mean	1.662
		std dev	0.111
		CV_2	0.067

$\overline{CV_2}$ 0.071

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Naphthalene, No. S292

OSHA Standard: 50 mg/cu m

Chemical used for Validation: Naphthalene, Fisher Scientific Company, certified

Procedure:

The general procedure used is described in NIOSH Method No. S292 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate amount of naphthalene represented in a 200-liter air sample. A solution of naphthalene in carbon disulfide was used for spiking in order to minimize any error and variability in weighing small amounts of the naphthalene crystals. Independent tests indicate that the presence of as much as 50 µl of carbon disulfide does not significantly affect desorption efficiency. The data are summarized in Table 1 for samples spiked with naphthalene in carbon disulfide and naphthalene crystals. All samples were allowed to equilibrate for at least overnight; there was also no apparent effect of sample age on desorption efficiency. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report and attachment.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples of naphthalene were generated by passing a controlled amount of dry air through a glass tower containing naphthalene crystals as shown schematically in Figure 1. The setup is a modified version of the vapor generation/dilution system described in the S47 Butyl Acetate Backup Data Report. The amount of dry air going through the naphthalene tower was adjusted by means of the needle valve until the desired mainline generator concentration equivalent to 2X OSHA standard test level was achieved; the total hydrocarbon analyzer was used to aid in this adjustment. The naphthalene tower was weighed before and after the actual generation period to determine the rate of feed into the system. For the set of samples reported, the naphthalene delivery rate was 7.16 mg/min into a dry air stream flowing at a rate of 0.0863 cu m/min. The

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TABLE 1

Comparison of DE: Solid Naphthalene
vs. Naphthalene in Solution

	Samples Spiked With					
	Solid Naphthalene			Naphthalene in Carbon Disulfide*		
Sample Age	mg added	mg found	DE	mg added	mg found	DE
1 day	11.05	8.55	0.774	9.99	7.66	0.767
1 day	10.66	8.31	0.780	9.99	7.68	0.769
1 day	10.82	8.33	0.770	9.99	7.60	0.761
5 days	10.73	8.43	0.786	9.99	7.58	0.759
5 days	12.69	10.44	0.823	9.99	7.86	0.787
5 days	12.43	9.45	0.760	9.99	7.60	0.761
		Average	0.782		Average	0.767

*A 50 µl aliquot was used for spiking.

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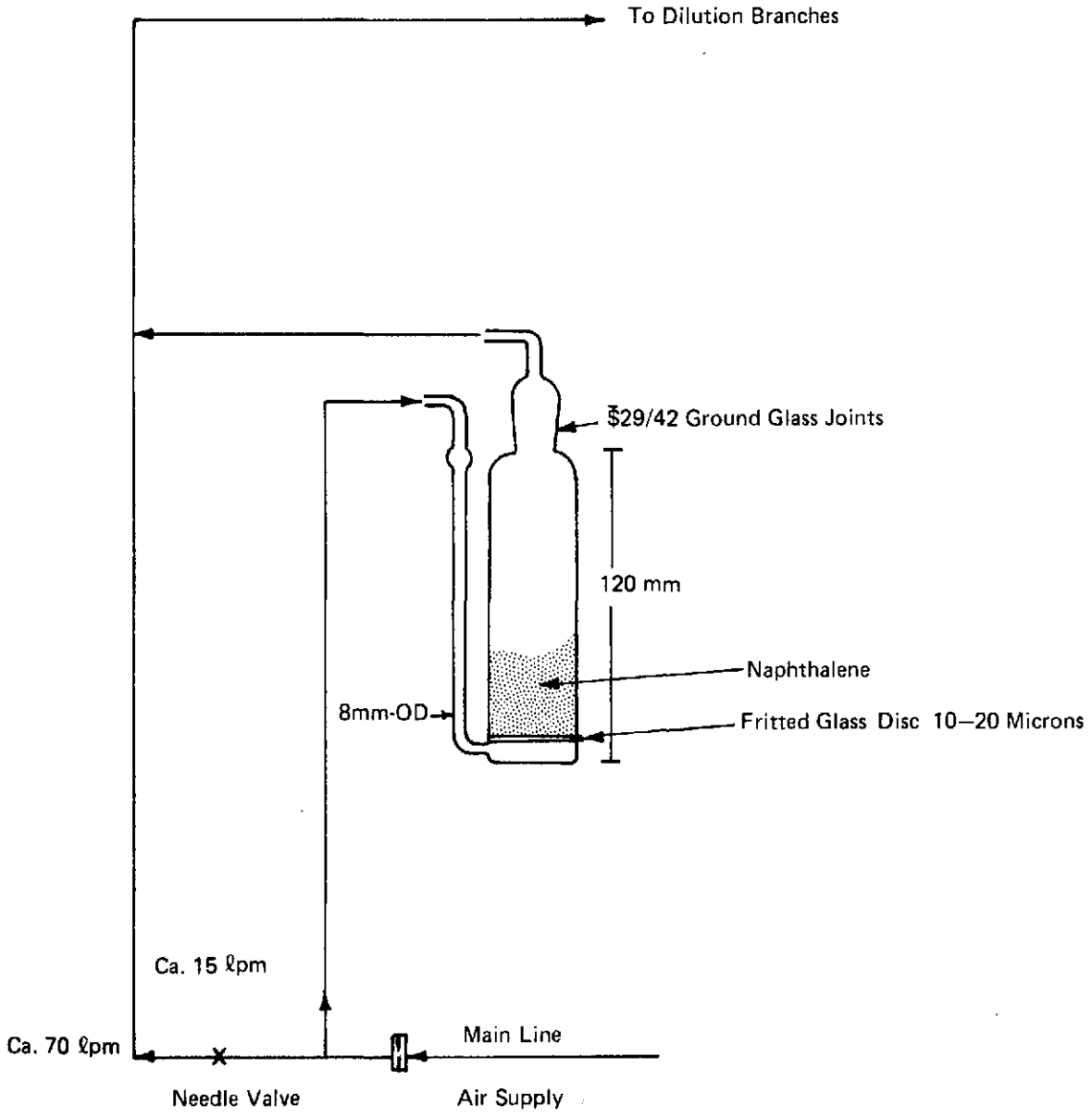

FIGURE 1 NAPHTHALENE GENERATOR

three sample lines were maintained at dilution ratios of 0.233, 0.475, and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 180 minutes (198 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report and attachment.

Breakthrough

The first section of the charcoal tube was found to hold at least 19.4 mg of naphthalene when a test atmosphere containing 81.1 mg/cu m of naphthalene in air was sampled at 1.0 liter per minute for 240 minutes; breakthrough was not observed at this time, i.e., the concentration of analyte in the effluent was less than 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0194$ $\overline{CV}_2 = 0.0204$ $\overline{CV}_T = 0.0546$

The average recovery of the generated samples over all levels was 97.4%.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Naphthalene, S292

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.96	3.55	0.716	9.92	7.43	0.749	19.73	15.74	0.798
4.96	3.60	0.726	9.92	7.58	0.764	19.73	16.27	0.825
4.96	3.51	0.708	9.92	7.59	0.765	19.73	15.74	0.798
4.96	3.57	0.720	9.92	7.91	0.797	19.73	16.49	0.836
4.96	3.52	0.710	9.92	7.39	0.745	19.73	15.89	0.805
4.96	3.56	0.718	9.92	7.45	0.751	19.73	16.34	0.828
n =		6			6			6
mean		0.716			0.762			0.815
std dev		0.0066			0.0191			0.0166
CV_1		0.0093			0.0250			0.0204

$\overline{CV_1}$ 0.0194

$\overline{CV_{A+\overline{DE}}}$ 0.0209

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Data Sheet: Naphthalene, S292

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.444	3.58	197.2	18.15	19.34	
	2.464	3.61	194.0	18.61	19.34	
	2.389	3.50	194.0	18.04	19.34	
	2.460	3.60	196.8	18.29	19.34	
	2.472	3.62	195.6	18.51	19.34	
	2.477	3.63	194.7	18.64	19.34	
			n = 6			
			mean	18.37		0.950
			std dev	0.250		
			CV_2	0.0136		
1S	5.47	7.25	195.9	37.0	39.4	
	5.97	7.91	197.0	40.2	39.4	
	5.86	7.76	199.4	38.9	39.4	
	5.89	7.80	198.2	39.4	39.4	
	5.84	7.74	195.8	39.5	39.4	
	5.93	7.85	195.9	40.1	39.4	
			n = 6			
			mean	39.2		0.995
			std dev	1.172		
			CV_2	0.0299		
2S	12.50	15.49	193.3	80.1	83.0	
	12.71	15.75	191.0	82.5	83.0	
	12.72	15.76	195.4	80.7	83.0	
	12.88	15.96	196.3	81.3	83.0	
	12.71	15.75	196.1	80.3	83.0	
	12.91	16.00	194.0	82.5	83.0	
			n = 6			
			mean	81.2		0.978
			std dev	1.063		
			CV_2	0.0131		
			$\overline{CV}_2$	0.0204		

Backup Data Report

Substance: Nicotine, No. S293

OSHA Standard: 0.5 mg/cu m

Chemical Used for Validation: Nicotine, Eastman Organic Chemicals, Highest purity

Procedure

The nicotine in air was collected by drawing 100 liters of air through a glass tube containing 100 mg of XAD-2 resin. The nicotine was desorbed from the resin with ethyl acetate and analyzed using a gas chromatograph equipped with an alkali-flame ionization detector. Gas chromatographic analyses were done using diphenylamine as internal standard. For every set of 18 samples analyzed, six independent standard solutions were used to calibrate instrument response for nicotine. A calibration curve was drawn by plotting the area ratio of the nicotine to that of the internal standard against concentration of nicotine. Details of the analytical procedure used are described in NIOSH Method No. S293.

Desorption efficiency tests were done by spiking with the appropriate volume of nicotine such that the amount added was equivalent to that present in a 100-liter air sample at 0.5, 1 and 2X OSHA standard. The resin used was XAD-2 supplied by Rohm and Haas, Philadelphia, PA. Spiking and desorption tests were done in 5-ml vials with Teflon-lined screw caps. Details on handling of XAD-2 resin may be found in the S264 Ethyl Silicate Backup Data Report. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Note that two sets of spiked samples were analyzed in order to test sample stability on storage. The data show no significant difference between samples stored for 1 day and 5 days.

Modification

The original collection medium suggested for nicotine was ethylene glycol in impingers. Experimental studies were initiated to test whether the preferred collection in a solid sorbent-packed tube could be used in place of the ethylene glycol/impinger. The data for the solid sorbents and solvents tested are summarized below.

DE on Selected Solid Sorbents

Solid Sorbent	Solvent	µg Added	DE
Lot 105 Charcoal	Carbon disulfide	194	0.52
Lot 105 Charcoal	Ether	194	0.51
Lot 104 Charcoal	Carbon disulfide	194	0.11
Lot 104 Charcoal	Ether	194	0.10
XAD-2	Carbon disulfide	194	1.02
XAD-2	Ethyl acetate	126	0.98

All the samples spiked with 194 µg of nicotine were analyzed using a flame ionization detector. This sample quantity is equivalent to a 200-liter sample at 2X OSHA standard. These studies indicated that the sensitivity of the FID would not be adequate for nicotine concentrations below the OSHA standard for a 200-liter sample. Thus all subsequent studies were carried out using an alkali-flame ionization detector for greater sensitivity as well as specificity. Ethyl acetate was used instead of carbon disulfide because the latter is not compatible with the alkali-FID.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard were generated by delivering nicotine via a syringe injector into a stream of dry air. The main line air stream flow was maintained at 0.101 cu m/min and the syringe injector was set to deliver 0.1 mg/min into the mainline. The low levels of nicotine being delivered made it difficult to accurately calibrate the syringe delivery rate by the normal weighing method. Likewise the FID response was too low to allow concentration measurements using the total hydrocarbon analyzer. However, since the collection efficiency has been established to be 100%, the values found in the collected samples serve as a measure of generator concentration. Note that the average values found for the 0.5, 1 and 2S test levels (Table 4) give the relative ratios of 0.249, 0.509 and 1.000. These ratios are in good agreement with the known dilution ratios of the generator based on air flow measurements--0.233, 0.486 and 1.000 respectively.

Breakthrough

The first section of the charcoal tube was found to hold at least 0.2 mg of nicotine when a test atmosphere containing 1.2 mg/cu m of nicotine in air was sampled at 1.1 liters per minute for 180 minutes. The data were obtained by analyzing duplicate samples collected at 1.1 liters per minute for 90, 120 and 180 minutes. The data are summarized in Table 1A based on the analysis of both front and backup sections of the sampling tubes. Similarly the front and backup sections of a complete set of six samples at 2X OSHA standard level for a 100-liter sample were analyzed. The data in Table 1B show no breakthrough in any of these samples.

Precision and Accuracy

The statistical procedures used are described in Reference 1. The statistical calculations were performed on the samples which had been stored.

$\overline{CV}_1 = 0.0149$ $\overline{CV}_2 = 0.0425$ $\overline{CV}_T = 0.0659$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Collection Efficiency on XAD-2 of Nicotine, S293

A. Samples collected at 0.8 liters per minute for 90, 120 and 180 minutes.

Sample Volume in Liters	μg Found			% Collection Efficiency
	Front	Backup	Total	
97	116.5	0	116.5	100
98	118.1	0	118.1	100
133	165.0	0	165.0	100
132	161.8	0	161.8	100
195	245.9	0	245.9	100
199	208.4	0	208.4	100

Average Collection Efficiency... 100%

B. Samples collected at 1.1 liters per minute for 90 minutes.

Sample Volume in Liters	μg Found*			% Collection Efficiency
	Front	Backup	Total	
99	106.8	0	106.8	100
99	118.1	0	118.1	100
99	121.3	0	121.3	100
99	119.7	0	119.7	100
99	116.5	0	116.5	100
99	118.1	0	118.1	100

Average Collection Efficiency... 100%

* Corrected for appropriate DE value.

TABLE 2

Data Sheet: Nicotine, S293

Analysis
(Samples stored for 1 day)

Level	0.5		1S			2S		
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
31.6	28.27	0.895	63.1	59.5	0.943	126.2	110.8	0.878
31.6	27.49	0.870	63.1	58.8	0.932	126.2	120.0	0.951
31.6	27.39	0.867	63.1	61.8	0.979	126.2	116.8	0.926
31.6	29.25	0.926	63.1	57.6	0.913	126.2	118.2	0.937
31.6	30.0	0.949	63.1	59.9	0.949	126.2	128.5	1.018
31.6	28.66	0.907	63.1	61.4	0.973	126.2	128.1	1.015
n =		6			6			6
mean		0.902			0.948			0.954
std dev		0.0320			0.0249			0.0542
CV_1		0.0354			0.0262			0.0568

$\overline{CV}_1$ 0.0415

$\overline{CV}_{A+\overline{DE}}$ 0.0448

TABLE 3

Data Sheet: Nicotine, S293

Analysis
(Samples stored for 5 days)

Level	0.5S		1S			2S		
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
31.6	33.40	1.057*	63.1	59.4	0.941	126.2	123.8	0.981
31.6	28.82	0.912	63.1	59.8	0.948	126.2	124.2	0.984
31.6	28.22	0.893	63.1	60.3	0.956	126.2	122.4	0.970
31.6	28.44	0.900	63.1	59.0	0.935	126.2	126.7	1.004
31.6	27.95	0.884	63.1	61.1	0.968	126.2	124.3	0.985
31.6	28.38	0.898	63.1	60.1	0.952	126.2	122.4	0.970
n =		5			6			6
mean		0.897			0.950			0.982
std dev		0.0102			0.0116			0.0125
CV_1		0.0114			0.0122			0.0128

$\overline{CV}_1$ 0.0122

$\overline{CV}_{A+\overline{DE}}$ 0.0132

*These values excluded from statistical analysis based on Grubb's test.

TABLE 4

Data Sheet: Nicotine, S293

Sampling and Analysis
(Samples stored for 5 days)

Test Level	Found			
	µg	Corr µg	Liters	µg/ℓ or mg/cu m
0.5S	24.71	27.76	97.9	0.284
	26.73	30.00	97.2	0.309
	25.61	28.78	97.6	0.295
	26.90	30.20	97.2	0.311
	25.10	28.20	98.4	0.287
	26.17	29.40	98.5	0.298
			n = 6	
			mean	0.297
			std dev	0.0111
			CV_2	0.0373
1S	50.5	53.4	95.2	0.561
	58.5	61.9	100.1	0.618
	55.0	58.2	97.1	0.599
	56.7	60.0	97.8	0.613
	57.6	61.0	98.1	0.622
	58.3	61.7	97.7	0.632
			n = 6	
			mean	0.608
			std dev	0.0252
			CV_2	0.0415
2S	104.1	106.8	98.3	1.086
	115.2	118.1	97.8	1.208
	118.3	121.3	96.5	1.257
	116.7	119.7	98.7	1.213
	113.6	116.5	96.8	1.204
	115.2	118.1	98.2	1.203
			n = 6	
			mean	1.195
			std dev	0.0572
			CV_2	0.0479
			$\overline{CV}_2$	0.0425

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Backup Data Report

Substance: Parathion, No. S295

OSHA Standard: 0.11 mg/cu m - skin

Chemicals Used for Validation: Aqua-8 Parathion (for generation of test atmospheres) FMC Corporation

Parathion, Analytical Reagent (for analytical validation) Monsanto

Procedure

The general procedure used is described in NIOSH Method No. S295. The reliability of the analytical method was tested at sample concentrations equal to that present in a 120-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot (2, 4, and 8 microliters) of a 3.3 mg/ml solution of parathion in iso-octane was added to 37-mm Type A glass fiber filters. Parathion was extracted from the filter with iso-octane and analyzed by gas chromatography using a flame photometric detector. Details of the extraction and analysis procedures may be found in Section 8.4 of NIOSH Method No. S295. Test atmospheres of parathion at concentrations of approximately 0.5, 1, and 2 times the OSHA standard were generated as described below. Six samples at each of the three concentrations were collected on glass fiber filters. The results of analysis of these samples are given in the Sampling and Analysis table. The estimated average size of the particles was one micron diameter.

Generation

Samples of parathion in air were generated by the procedure described in Reference No. 1. However, the aspirator output was divided by means of a splitter prior to entry into the dilution system. This was necessary to generate the proper concentration levels in the generator system.

A 0.5% solution of parathion in toluene (6.25 ml of Aqua-8 Parathion which contains 80% of parathion made up to a 1-liter volume with toluene) was used in the aspiration system for the generation of parathion.

To obtain samples at the desired concentration, a set of generation conditions was chosen, several samples collected for at least ten minutes, and these samples analyzed. The results of the analyses were used to select conditions to reach the required concentration. When the desired concentration was reached, six samples at each of the three levels were collected simultaneously using the three-stage dilution system described in Reference No. 2. Samples were collected for 80 minutes at approximately 1.5 liter/minute.

Collection Efficiency

Collection efficiency tests were conducted at 0.2643 mg/cu m (as determined by analysis of samples collected at 2X the OSHA standard level) by mounting in series two filters in direct contact with each other and a midget bubbler containing 15 ml of iso-octane. The results of the collection efficiency test are given below:

mg/cu m found first filter	mg/cu m found backup filter	mg/cu m found backup bubbler	Collection Efficiency
0.2802	N.D. *	N.D. *	1.00
0.2743	"	"	1.00
0.2534	"	"	1.00
0.2509	"	"	1.00
0.2558	"	"	1.00
0.2712	"	"	1.00

* N.D. = not detected at a detection limit of 3.48×10^{-5} mg/cu m.

Since collection efficiency was determined to be 1.00, no correction for collection efficiency is needed in this method.

Discussion

The following experiment was conducted to ascertain whether filter collection would be appropriate for the collection of parathion.

Two filters were spotted with 4 µl of a stock solution of parathion in iso-octane containing 3.3 mg/ml. After spiking, the filters were placed in the filter cassettes; each was connected in series with a midget bubbler containing 15 ml of iso-octane. Air was pulled through the two filter-bubbler combination at a flow rate of 1 liter per minute for two hours. The filter and bubbler were then analyzed for parathion. The results are given below:

mg spiked onto filter	mg found on filter	mg found in bubbler	% Recovery on filter
0.0132	0.0128	0.0004	97.0
0.0132	0.0134	0.0004	101.5
		mean	99.2

From these results, it was concluded that the analyte would be present as a particulate, it would not be vaporized from the filter after collection, and filter collection was selected.

During sample collection, a backup support pad was not needed in holding the filter in place, but it is recommended that one should be used.

A time study was conducted by spiking six glass fiber filters and allowing them to stand for one week before analysis. The time study was conducted at 1X the OSHA standard level using 4 µl of a stock solution of parathion in iso-octane (3.3 mg/ml). The filters were extracted with 15 ml of iso-octane and analyzed by GC equipped with a flame photometric detector. The results given below were compared with the 1X data in the Analysis table which represents samples which were analyzed immediately.

mg taken	mg found	Recovery
0.0132	0.0122	0.924
0.0132	0.0132	1.000
0.0132	0.0130	0.985
0.0132	0.0132	1.000
0.0132	0.0131	0.992
0.0132	0.0133	1.008
	mean	0.985
	std dev	0.030

From the above results, parathion is stable on glass fiber filters for at least one week.

Precision and Accuracy

The statistical procedures are described in Reference No. 3.

$\overline{CV}_1 = 0.015$ $\overline{CV}_2 = 0.059$ $\overline{CV}_T = 0.078$

Data Sheet: Parathion S295

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.0066	0.0067	1.015	0.0132	0.0128	0.970	0.0264	0.0261	0.989
0.0066	0.0067	1.015	0.0132	0.0128	0.970	0.0264	0.0267	1.011
0.0066	0.0066	1.000	0.0132	0.0133	1.008	0.0264	0.0267	1.011
0.0066	0.0067	1.015	0.0132	0.0132	1.000	0.0264	0.0270	1.023
0.0066	0.0066	1.000	0.0132	0.0134	1.015	0.0264	0.0265	1.004
0.0066	0.0067	1.015	0.0132	0.0129	0.977	0.0264	0.0271	1.026
n =		6			6			6
mean		1.010			0.990			1.011
std dev		0.008			0.020			0.013
CV_1		0.008			0.020			0.013

$\overline{CV}_1$ 0.015

$\overline{CV}_{A+\overline{AMR}}$ 0.016

Data Sheet: Parathion S295

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.0082	116.0	0.0707
	0.0090	110.4	0.0815
	0.0091	113.6	0.0801
	0.0080	117.6	0.0680
	0.0077	113.6	0.0678
	0.0080	118.0	0.0678
		n = 6	
		mean	0.0726
		std dev	0.0064
		CV_2	0.088
1S	0.0180	115.6	0.1557
	0.0172	111.2	0.1547
	0.0174	111.6	0.1559
	0.0179	113.6	0.1576
	0.0165	106.4	0.1551
	0.0173	116.0	0.1491
		n = 6	
		mean	0.1547
		std dev	0.0029
		CV_2	0.019
2S	0.0343	122.4	0.2802
	0.0327	119.2	0.2743
	0.0299	118.0	0.2534
	0.0285	113.6	0.2509
	0.0307	120.0	0.2558
	0.0307	113.2	0.2712
		n = 6	
		mean	0.2643
		std dev	0.0124
$\overline{CV}_2$ 0.059		CV_2	0.047

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

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References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Thallium, Soluble Compounds as Tl, No. S306

OSHA Standard: 0.1 mg/cu m

Chemical Used for Validation: Thallium Sulfate, Tl_2SO_4, Fisher Scientific Company, purified

Procedure

The general procedure used is described in NIOSH Method No. S306 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to those present in a 540-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of an aqueous solution of the analyte was added to 37-mm Type AA Millipore filters. The sample-containing filters were digested with concentrated nitric acid and diluted to volume with water. Analyses were done with a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer with an EDL lamp for thallium. The absorbance, measured at 276.8 nm was used as a measure of the thallium concentration in the sample. Appropriate standard solutions were analyzed on the same day the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S306.

Modification

There was no major modification of P&CAM 173, except that hydrochloric acid was not added after the filter digestion process. It should be noted that the filter digestion route is recommended, in spite of the categorical classification as soluble thallium compounds, because experiments conducted using either a cold or hot water extraction procedure gave low recoveries of 70% and 67% respectively when thallium sulfate was used. The use of hot water with ultrasonic agitation proved to be detrimental rather than helpful, yielding an average recovery of 54%. This lower recovery is probably due to the fact that the ultrasonic agitation process tends to disintegrate the filter, thus increasing the total surface area upon which the thallium can get adsorbed. Each set of data was based on treatment of triplicate filters each containing 54 µg of thallium.

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of thallium sulfate containing 1.2 g/liter as thallium into a dry solvent-free air stream flow. The atomizer flow rate was 9 liters per minute;

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aerosol from the atomizer was diluted with 84 liters per minute of dry solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 360 minutes (540 liters) at 22°C and 759 mm Hg atmospheric temperature and pressure. Since collection efficiency was found to be 1.00 $\pm$ 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate thallium was determined by collecting six filter samples at an air sample concentration of 0.15 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency was 99.1% when the test atmosphere was sampled for 360 minutes at 1.5 liters per minute (Table 1).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0149$ $\overline{CV}_2 = 0.0334$ $\overline{CV}_T = 0.0604$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Collection Efficiency: Thallium, Soluble Compounds as Tl, S306

μg Found			
Front	Backup	Total	% Collected in Front
81.4	0.50	81.90	99.4
77.3	1.30	78.60	98.3
81.5	0.55	82.05	99.3
84.2	0.65	84.85	99.2
84.0	0.65	84.65	99.2
83.4	0.97	84.37	98.9

Average Collection Efficiency.... 99.1 ± 0.40%

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Data Sheet: Thallium, Soluble Compounds as Tl, S306

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
26.4	25.7	0.973	54.0	53.5	0.991	108.0	108.5	1.005
26.4	25.4	0.962	54.0	53.6	0.993	108.0	108.6	1.006
26.4	26.7	1.011	54.0	54.2	1.004	108.0	108.4	1.004
26.4	26.7	1.011	54.0	53.7	0.994	108.0	108.0	1.000
26.4	27.1	1.027	54.0	53.7	0.994	108.0	109.3	1.012
26.4	26.2	0.992	54.0	53.6	0.993	108.0	109.4	1.013
n =		6			6			6
mean		0.996			0.995			1.007
std dev		0.0249			0.0046			0.0050
CV_1		0.0250			0.0046			0.0049

$\overline{CV}_1$ 0.0149

$\overline{CV}_{A+\overline{DE}}$ 0.0161

Data Sheet: Thallium, Soluble Compounds as Tl, S306

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	18.48	546	0.0338
	18.58	544	0.0342
	19.55	542	0.0361
	18.78	544	0.0345
	18.48	543	0.0340
	17.75	561	0.0316
		n = 6	
		mean	0.0340
		std dev	0.0014
		CV_2	0.0426
1S	38.8	546	0.0711
	38.7	547	0.0707
	37.9	544	0.0697
	40.3	548	0.0735
	39.3	551	0.0713
	40.6	548	0.0741
		n = 6	
		mean	0.0717
		std dev	0.0017
		CV_2	0.0238
2S	81.4	546	0.1491
	77.3	546	0.1416
	81.5	546	0.1493
	84.2	546	0.1542
	84.0	545	0.1541
	83.4	550	0.1516
		n = 6	
		mean	0.1500
		std dev	0.0047
		CV_2	0.0311
		$\overline{CV}_2$	0.0334

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Backup Data Report

Substance: Arsenic and Compounds (as As), No. S309

OSHA Standard: 0.5 mg/cu m

Chemical Used for Validation: As_2O_3 NBS 83a

Procedure

The general procedure is described in NIOSH Method No. S309 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations representing 85-liter samples at 0.5, 1.0, and 2.0 times the OSHA standard. The appropriate aliquot of a solution of arsenic in dilute sodium hydroxide was added to 37-mm, 0.8-micron Type AA Millipore filters. The filters containing the samples were digested with concentrated nitric and perchloric acids and the analyte dissolved in dilute nitric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer equipped with a heated graphite atomizer, HGA Model 2000 and Deuterium Background Corrector. The absorbance, measured at 193.7 nm, was used as a measure of the arsenic concentration in the sample. A similar procedure was used for the analysis of 18 generated samples, 6 each at approximately 0.5, 1, and 2 times the OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S309.

Modification

P&CAM 173 was modified by use of perchloric acid to aid in decomposition of the filter and by the use of a heated graphite atomizer furnace accessory to the atomic absorption spectrophotometer.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the Nickel report (Reference No. 1). Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing solutions of arsenic in dilute sodium hydroxide at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of approximately 1.4 liters per minute for 60 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate arsenic was determined by collecting eight filter samples

at an air sample concentration of 1 mg/cu m (2X OSHA standard level). The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was considered to be 1.00 when the test atmosphere was sampled for 60 minutes. The data on the backup filter were obtained on a final assay solution volume of 5 ml rather than 100 ml as recommended in the NIOSH Method S309. No correction for collection efficiency is necessary.

COLLECTION EFFICIENCY

2X level

Front Filter Found μg	Backup Filter Found μg	Collection Efficiency
91.3	N.D.	1.00
87.7	N.D.	1.00
88.8	N.D.	1.00
83.3	N.D.	1.00
88.8	N.D.	1.00
83.3	N.D.	1.00
90.0	N.D.	1.00
85.5	N.D.	1.00

N.D. = Not detected (< 0.5 μg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.038$ $\overline{CV}_2 = 0.025$ $\overline{CV}_T = 0.058$

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Data Sheet: Arsenic and Compounds (as As) S309

Analysis

Level	0.5S		1S			2S		
mg added	mg found	A.M.R.	mg added	mg found	A.M.R.	mg added	mg found	A.M.R.
0.0150	0.0156	1.040	0.0300	0.0300	1.000	0.0600	0.0650	1.083
0.0150	0.0167	1.113	0.0300	0.0310	1.033	0.0600	0.0645	1.075
0.0150	0.0156	1.040	0.0300	0.0317	1.057	0.0600	0.0620	1.033
0.0150	0.0161	1.073	0.0300	0.0325	1.083	0.0600	0.0620	1.033
0.0150	0.0172	1.147	0.0300	0.0300	1.000	0.0600	0.0645	1.075
0.0150	0.0172	1.147	0.0300	0.0325	1.083	0.0600	0.0670	1.117

n =	6	6	6
mean	1.093	1.043	1.069
std dev	0.049	0.038	0.032
CV_1	0.045	0.036	0.030

$\overline{CV}_1$ 0.038

$\overline{CV}_{A+\overline{AMR}}$ 0.041

An average Analytical Method Recovery (A.M.R.) of 1.068 was used to calculate the corr. mg in the Sampling and Analysis Table.

Data Sheet: Arsenic and Compounds (as As) S309

Sampling and Analysis

Test Level	Found			
	mg	Corr mg	Liters	mg/cu m*
0.5S	0.0176	0.0165	84.6	0.1950
	0.0174	0.0163	83.8	0.1945
	0.0178	0.0167	84.1	0.1986
	0.0178	0.0167	83.8	0.1993
	0.0178	0.0167	83.2	0.2007
	0.0181	0.0169	83.6	0.2022
			n = 6	
			mean	0.1984
			std dev	0.0031
			CV_2	0.016
1S	0.0440	0.0412	82.7	0.498
	0.0440	0.0412	82.1	0.502
	0.0475	0.0445	83.1	0.536
	0.0460	0.0431	84.0	0.513
	0.0475	0.0445	82.1	0.542
	0.0475	0.0445	83.5	0.533
			n = 6	
			mean	0.521
			std dev	0.019
			CV_2	0.036
2S	0.0845	0.0791	84.6	0.935
	0.0800	0.0749	83.8	0.894
	0.0800	0.0749	84.1	0.891
	0.0800	0.0749	83.8	0.894
	0.0813	0.0761	83.6	0.910
	0.0800	0.0749	83.6	0.896
			n = 6	
			mean	0.903
			std dev	0.017
$\overline{CV}_2$ 0.025			CV_2	0.019

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

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References

1. Backup Data Report, Nickel, No. S206, prepared under NIOSH Contract No. CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract No. CDC-99-74-45.

Backup Data Report

Substance: Aniline, No. S310

OSHA Standard: 5 ppm (19 mg/cu m) - skin

Chemical used for Validation: Aniline
J. T. Baker Chemical Company

Procedure

The procedure for collecting and analyzing concentrations of aniline in air is described in NIOSH Method S310, which has been adapted from P&CAM 168. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking approximately 150-mg portions of silica gel* with appropriate amounts of aniline to represent 20-liter air samples. Samples of aniline were generated by a syringe drive system and collected in silica gel tubes. The analyte was desorbed with 95% ethanol in an ultrasonic bath for one hour and analyzed by gas chromatography using an automatic sample injector. The amounts measured were corrected for D.E. to determine corrected mg. The concentration in air "found" was determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 113.5 minutes). The "true" concentration at the 2X, 1X, and 0.5X OSHA standard levels were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. A total hydrocarbon analyzer was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were three major modifications made to P&CAM 168.

1. The analyte was collected in 7-cm long by 4-mm I.D. silica gel tubes containing 150 mg of 20/40 mesh silica gel in the adsorbing section and 75 mg in the backup section instead of the 12.5-cm long by 8-mm I.D. tubes containing 700 mg of 45/60 mesh silica gel in the adsorbing section and 150 mg in the backup section.

2. A solution of aniline in a benzene-hexane mixed solvent was used to apply the analyte to the silica gel for desorption efficiency determinations. The solution was prepared by dissolving 1 ml aniline in 2 ml benzene in a 10-ml volumetric flask, and bringing to volume with hexane. The concentration of aniline was 102.2 mg/ml in this solution, requiring 2, 4, and 8 µl injections onto the silica gel for the 0.5X, 1X, and 2X OSHA levels. The mixed solvent was used, because aniline was not sufficiently miscible with hexane at the concentration required.

3. Desorption was done for one hour in an ultrasonic bath to aid the desorption process.

* Silica gel tubes were obtained from Environmental Compliance Corp.

Generation

Samples of aniline were generated with a calibrated automated syringe drive pump (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with aniline and placed in the syringe drive pump. The syringe, which was attached to a 15-inch long stainless steel needle, delivered the analyte into a heated glass tube at a rate of 1.99 mg/minute. The tube was packed with glass beads to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen at 7.7 liters/minute and diluted with air at a rate of 44.4 liters/minute to obtain the 2X concentration level. Further dilution with air was made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The total hydrocarbon analyzer was used to monitor the constancy of the concentrations in the three chambers during sampling.

Samples were collected for 113.5 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the silica gel tube was conducted as described in Reference No. 2. A total hydrocarbon analyzer was used to monitor the pump effluent. Less than 5% of the generated concentration of 38.2 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.20 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

The 7-cm long x 4-mm I.D. silica gel tubes were used instead of the 12.5-cm long x 8-mm I.D. tubes recommended in P&CAM 168, because the pressure drop across the larger tubes, which were packed with a finer mesh silica gel, was too great.

A time study was conducted to determine the recovery of aniline on silica gel when added from a vapor phase. Six samples at each of the three OSHA levels were generated using the syringe drive pump as described under the Generation Section. Three of the samples were flushed with nitrogen and capped after sampling, and three were capped tightly with the supplied plastic caps from the silica gel tubes. The samples were allowed to stand for one week before analysis. The samples were desorbed with 95% ethanol for one hour in an ultrasonic bath. The results are given on the following page.

TIME STUDY RESULTS OF ANILINE

	Found				Taken	
	mg found	corr. mg	Liters	mg/cu m	mg/cu m	Recovery(%)
			(FLUSHED WITH NITROGEN)			
0.5X	0.1876	0.1924	21.84	8.81	9.54	
	0.2047	0.2089	23.55	8.87	9.54	
	0.1949	0.1995	22.64	8.81	9.54	
			mean	8.83		92.6
1X	0.305	0.307	17.52	17.52	19.08	
	0.343	0.345	19.45	17.74	19.08	
	0.359	0.362	20.13	17.98	19.08	
			mean	17.75		93.0
2X	0.768	0.773	21.16	36.5	38.2	
	0.748	0.753	20.48	36.8	38.2	
	0.711	0.715	20.13	35.5	38.2	
			mean	36.3		95.0
			(NOT FLUSHED WITH NITROGEN)			
0.5X	0.1973	0.2017	22.86	8.82	9.54	
	0.1854	0.1904	21.84	8.72	9.54	
	0.1862	0.1912	21.38	8.94	9.54	
			mean	8.83		92.6
1X	0.348	0.350	19.79	17.68	19.08	
	0.349	0.351	19.68	17.84	19.08	
	0.334	0.336	19.00	17.68	19.08	
			mean	17.73		92.9
2X	*0.773	0.778	19.11	40.7	38.2	
	0.776	0.781	21.27	36.7	38.2	
	0.762	0.767	20.93	36.6	38.2	
			mean	36.6		95.8

* This value was deleted, because the sample was contaminated.

The equation D.E. = $0.994 - e^{-20.99 \times \text{mg found}}$ was used to calculate corr. mg in the above table.

From the above results, aniline is stable on silica gel for at least one week without flushing with nitrogen.

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Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.013$ $\overline{CV}_2 = 0.032$ $\overline{CV}_T = 0.060$

The average recovery at the OSHA standard level was 95.3%.

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Aniline S310

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.2044	0.1939	0.949	0.409	0.403	0.985	0.818	0.806	0.985
0.2044	0.1982	0.970	0.409	0.407	0.995	0.818	0.808	0.988
0.2044	0.2005	0.981	0.409	0.406	0.993	0.818	0.808	0.988
0.2044	0.2034	0.995	0.409	0.415	1.015	0.818	0.814	0.995
0.2044	0.2011	0.984	0.409	0.415	1.015	0.818	0.809	0.989
0.2044	0.2040	0.998	0.409	0.407	0.995	0.818	0.799	0.977
n =		6			6			6
mean		0.980			1.000			0.987
std dev		0.018			0.012			0.006
CV_1		0.018			0.012			0.006

$\overline{CV}_1$ 0.013

$\overline{CV}_{A+\overline{DE}}$ 0.014

The equation D.E. = $0.994 - e^{-20.99 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Aniline S310

Sampling and Analysis

Test Level

	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery (%)
0.5S	0.1964	0.2008	21.79	9.22	9.54	
	0.2116	0.2155	23.49	9.17	9.54	
	0.1819	0.1871	22.59	8.28	9.54	
	0.1813	0.1865	21.79	8.56	9.54	
	0.1785	0.1840	21.34	8.62	9.54	
	0.1950	0.1996	22.81	8.75	9.54	
			n = 6			
			mean	8.77		91.9
			std dev	0.37		
			CV_2	0.042		
1S	0.348	0.350	19.75	17.72	19.08	
	0.355	0.358	19.64	18.23	19.08	
	0.316	0.318	17.48	18.19	19.08	
	*0.382	0.385	18.95	20.32	19.08	
	0.351	0.353	19.41	18.19	19.08	
	0.370	0.373	20.09	18.57	19.08	
			n = 5			
			mean	18.18		95.3
			std dev	0.30		
			CV_2	0.016		
2S	0.658	0.662	19.07	34.7	38.2	
	0.781	0.786	21.22	37.0	38.2	
	0.789	0.794	21.11	37.6	38.2	
	0.758	0.763	20.88	36.5	38.2	
	0.770	0.775	20.43	37.9	38.2	
	0.742	0.746	20.09	37.1	38.2	
			n = 6			
			mean	36.8		96.3
			std dev	1.1		
$\overline{CV}_2$	0.032		CV_2	0.030		

* This value did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Benzene, No. S311
OSHA Standard:	Ceiling - 25 ppm Peak - 50 ppm 8-hr. T.W.A. - 10 ppm
Chemical Used for Validation:	Benzene, A.R. Mallinckrodt

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of benzene in air is described in NIOSH Method S311, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA ceiling standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of benzene to represent 2-liter air samples. Samples of benzene in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The temperature and pressure were 24°C and 762 mm Hg. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of benzene in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample x 10 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA ceiling standard levels were determined using bag standards and a total hydrocarbon analyzer. The total hydrocarbon analyzer was also used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

One major modification was made to P&CAM 127. A hexane solution of benzene containing 43.9 μg/μl was used to apply the analyte onto the charcoal. This was done so it would not be necessary to inject less than 2 μl at the 0.5X level.

Generation

Samples of benzene were generated by the procedure described in Reference No. 1 using the 2-piece vapor generator. The generator conditions used are given below:

Nitrogen flow rate:	62.2 ml/min at 24°C
Dilution air flow rate:	40.1 liter/min. at 24°C

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using bag standards and comparing the bag standard response with the chamber responses on the total hydrocarbon analyzer.

Samples were collected for 10 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test.

The breakthrough test was conducted at a concentration of 149.1 mg/cu m. Less than 5% of the generated concentration of 149.1 mg/cu m was present in the effluent after four hours of sampling at a rate of approximately 0.19 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.036$ $\overline{CV}_2 = 0.028$ $\overline{CV}_T = 0.059$

The average recovery at the OSHA ceiling standard level was 100.8%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Benzene S311

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	DE	µg taken	µg found	DE	µg taken	µg found	DE
87.9	88.6	1.008	175.7	175.3	0.998	351	337	0.960
87.9	75.5	0.859	175.7	170.2	0.969	351	346	0.986
87.9	84.2	0.958	175.7	171.6	0.977	351	347	0.989
87.9	87.0	0.990	175.7	171.8	0.978	351	344	0.980
87.9	87.2	0.992	175.7	175.6	0.999	351	348	0.991
87.9	86.0	0.978	175.7	163.4	0.930	351	349	0.994
n =		6			6			6
mean		0.964			0.975			0.983
std dev		0.054			0.025			0.012
CV_1		0.056			0.026			0.012

$\overline{CV}_1$ 0.036

$\overline{CV}_{A+\overline{DE}}$ 0.039

The equation D.E. = $0.983 - e^{-43.3 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Benzene S311

Sampling and Analysis

Test Level	Found					Taken	
	mg	Corr mg	Liters	mg/cu m	ppm*	ppm	Recovery (%)
0.5S	0.0759	0.0802	1.96	40.9	12.7	13.0	
	0.0763	0.0807	2.01	40.1	12.5	13.0	
	0.0723	0.0770	2.06	37.4	11.6	13.0	
	0.0696	0.0745	1.92	38.8	12.1	13.0	
	0.0638	0.0693	1.71	40.5	12.6	13.0	
	Sample was lost due to malfunctioning orifice.						
			n = 5				
			mean		12.3		94.6
			std dev		0.45		
			CV_2		0.037		
1S	0.1453	0.1481	1.70	87.1	27.1	25.9	
	0.1564	0.1593	1.88	84.7	26.3	25.9	
	0.1295	0.1323	1.57	84.3	26.2	25.9	
	0.1341	0.1368	1.70	80.5	25.0	25.9	
	0.1457	0.1485	1.73	85.8	26.7	25.9	
	0.1425	0.1453	1.79	81.2	25.3	25.9	
			n = 6				
			mean		26.1		100.8
			std dev		0.8		
			CV_2		0.031		
2S	0.334	0.340	2.00	170.0	52.9	51.8	
	0.330	0.336	1.95	172.3	53.6	51.8	
	0.312	0.317	1.85	171.4	53.3	51.8	
	0.314	0.319	1.85	172.4	53.6	51.8	
	0.314	0.319	1.85	172.4	53.6	51.8	
	Sample was lost due to malfunctioning orifice.						
			n = 5				
			mean		53.4		103.1
			std dev		0.3		
$\overline{CV}_2$	0.028		CV_2		0.006		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Cadmium Dust, No. S312

OSHA Standard: 0.2 mg/cu m (8-hour time-weighted average)
0.6 mg/cu m (Ceiling)

Chemical Used for Validation: Cadmium Oxide, Fisher Scientific, certified

Procedure

The general procedure used is described in NIOSH Method No. S312 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 15-liter sample at 0.5, 1 and 2 times the OSHA acceptable ceiling concentration. The 18 analytical samples were prepared by adding known aliquots of an aqueous solution of cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$, to a series of 37-mm Type AA Millipore filters. (Refer to discussion section for justification of this approach.) The sample-containing filters were digested with concentrated nitric acid and the analyte was solubilized by heating with hydrochloric acid. Analyses were done with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a hollow cathode lamp for cadmium and a 3-slot burner. The absorbance, measured at 228.8 nm, was used as a measure of the cadmium concentration in the sample. Appropriate standard solutions, prepared from commercially available 1000 ppm cadmium stock standard, were analyzed on the same day the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S312.

The cadmium oxide powder as supplied by Fisher was too coarse and was pulverized to finer particles for use in this validation study. A slurry of the cadmium oxide powder in methanol was ground in a ball-mill for 6 hours, dried at 115°C to constant weight, and the agglomerated particles were further broken up in an agate mortar to form a uniform powder. Microscopic examination of the powder showed that the particle size was 1-2 microns. This batch was used for all generated sample studies.

Modification

There was no major modification of P&CAM 1973.

Generation

The system used for generating dust atmospheres is described in Appendix A.

The target concentration of cadmium dust (0.3 to 1.2 mg/cu m) could not be produced when the pure cadmium oxide powder (1-2 microns) was loaded into the dust container. The lowest concentration which could be produced was approximately 10 mg/cu m at the slowest gear setting. Thus, the cadmium oxide powder was mixed with ferric oxide powder to produce a homogeneous mixture in the ratio of 1 part cadmium oxide to 14 parts ferric oxide by weight. Ferric oxide was chosen because it is available in the right particle size, it is soluble in acid, its specific gravity (8.1) is close enough to cadmium oxide (5.2) thus minimizing the chances of partitioning in the generator chamber, and it does not interfere with the cadmium assay as verified in the discussion section.

The cadmium oxide-ferric oxide mixture (1:14) was loaded into the dust container in a series of roughly one gram quantities. After each addition the powder was spread out to produce a layer of uniform thickness, and it was then compressed lightly (about 300 lbs) with a laboratory press. The concentration of the cadmium dust in the chamber was controlled by proper adjustment of the dust holder advance rate, and the three test level concentrations were generated independently. Although 12 samples can be collected simultaneously, only six samples for each test level were collected and analyzed. Samples were collected at 1.7 liters per minute for 15 minutes (25 liters). Since collection efficiency was found to be 1.00 $\pm$0.01, the concentrations in the generator and the "found" concentration were considered to be equal.

Discussion

An aqueous solution of cadmium nitrate was used for preparing the 18 analytical samples because the microgram amounts of cadmium oxide which must be added to the filters could not be weighed accurately. However, the analytical method was tested using weighable amounts of cadmium oxide. Six samples were prepared by weighing cadmium oxide in Ta-boats and adding a 37-mm filter to each of the weighed samples of cadmium oxide. These samples were then digested and analyzed as described. The data for these samples reported as µg cadmium and summarized below show an average recovery of 102% with a precision of 2.9%.

µg Cd Added	µg Cd Found	% Recovery
532	529	99.4
361	378	104.7
434	460	106.0
1581	1575	99.6
665	687	103.3
917	913	99.6
	Average	102.1%
	CV	2.9%

The data for the 18 analytical samples are summarized in Table 1. The average recovery was 105% with a coefficient of variation of 3.3%.

Studies were also conducted to verify that the ferric oxide chosen for "diluting" the cadmium oxide powder does not interfere with the AA analysis of cadmium. Sample solutions were prepared by mixing Cd and Fe in varying amounts and relative ratios; all solutions were in 25 ml of 0.5 N HCl. AA analysis of these solutions show that the absorbances of the sample solutions of Cd with Fe are identical to corresponding control solutions of Cd. These data are shown in Table 2.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for cadmium dust was determined by collecting six filter samples at an air sample concentration of 0.98 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency found was 100% when a test atmosphere containing 0.98 mg/cu m was sampled for 15 minutes (Table 3).

Precision and Accuracy

The statistical procedures used are described in Reference 1; the data are shown in Tables 1 and 4.

$\overline{CV}_1 = 0.0328$ $\overline{CV}_2 = 0.0385$ $\overline{CV}_T = 0.0645$

Since the collection efficiency was found to be 100% and no bias was found in the analytical recovery studies, average recovery = 105%, $\overline{CV}_T$ is a satisfactory measure of both precision and accuracy.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Data Sheet: Cadmium Dust, S312

Analysis*

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
4.52	4.70	1.040	9.04	9.13	1.010	18.07	18.65	1.032
4.52	4.62	1.022	9.04	9.30	1.029	18.07	18.47	1.022
4.52	4.52	1.000	9.04	9.40	1.040	18.07	18.70	1.035
4.52	4.70	1.040	9.04	9.95	1.101	18.07	18.65	1.032
4.52	5.00	1.106	9.04	9.87	1.092	18.07	19.00	1.051
4.52	5.00	1.106	9.04	9.87	1.092	18.07	19.00	1.051
n =		6			6			6
mean		1.052			1.061			1.037
std dev		0.0441			0.0390			0.0116
CV_1		0.0419			0.0367			0.0112

$\overline{CV_1}$ 0.0328

$\overline{CV_{A+\overline{DE}}}$ 0.0354

* All data are based on the analysis of filters spiked with known aliquots of a stock solution of cadmium nitrate.

TABLE 2

Effect of Iron on the Analysis of Cadmium

µg Cd Added	Fe Present: Cd to Fe Ratio	Fe Present: Absorbance	Fe Absent Absorbance
7.5	1:22	0.032	0.032
15.00	1:6	0.066	0.067
	1:11	0.067	
	1:22	0.065	
30.00	1:6	0.138	0.138

TABLE 3

Collection Efficiency of Cadmium Dust, S312
on 37-mm Type AA Millipore Filter

------- mg Found -------			% Collected
Front	Backup	Total	in Front
26.02	ND	26.02	100
25.68	ND	25.68	100
25.80	ND	25.80	100
25.55	ND	25.55	100
24.85	ND	24.85	100
24.48	ND	24.48	100

Average Collection Efficiency...100%

ND = Not detectable; the detection limit was
0.35 µg in a 25-ml solution.

TABLE 4

Data Sheet: Cadmium Dust, S312

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	3.10	25.65	0.1209
	3.20	26.03	0.1229
	3.40	26.07	0.1304
	3.20	26.25	0.1219
	3.27	26.45	0.1236
	3.13	25.73	0.1216
		n = 6	
		mean	0.1236
		std dev	0.00349
		CV_2	0.0282
1S	13.68	26.26	0.521
	13.15	25.50	0.516
	13.08	25.90	0.505
	11.62	26.09	0.445
	13.25	26.09	0.508
	12.68	25.57	0.496
		n = 6	
		mean	0.498
		std dev	0.0276
		CV_2	0.0554
2S	26.02	26.31	0.989
	25.68	25.55	1.005
	25.80	25.97	0.993
	25.55	26.14	0.977
	24.85	26.34	0.943
	24.48	25.62	0.956
		n = 6	
		mean	0.977
		std dev	0.0236
		CV_2	0.0242
		$\overline{CV}_2$	0.0385

Appendix A

Description of Dust Atmosphere Generation Apparatus

The basic elements of the system used to generate the dust test atmospheres are shown in Figures 1 and 2. The system consists of a Wright Dust Feeder, an aerosol charge neutralizer, and an 80-liter stainless dust chamber.

Dust samples to be dispersed in the apparatus are compressed into a container which is attached to the Wright Dust Feeder. In operation, the container and the dust compact are slowly rotated and driven against a stationary scraper blade by an electrically-operated mechanism. The blade continuously removes dust from the compact surface at a uniform rate. Compressed air enters the container and entrains the dust particles. The dust holder advance rate may be varied by changing the gears in the drive mechanism to provide a wide range of dust concentrations.

A short distance downstream of the dust feeder there is an auxiliary port for introducing additional air for further dilution of the dust cloud. Normally, a flow of 30 liters per minute is passed through the dust feeder itself, and dilution air is added at the rate of 70 liters per minute. Air flow rates are read from calibrated rotameters. Compressed air is supplied to the apparatus from the house compressed air system. This air is dried by passing it through a silica gel bed and then through a high efficiency fibrous filter and a membrane filter to remove particulate matter.

Since dust particles may accumulate electric charges in the dispersal process, the dispersed dust is passed through a charge neutralizer (Thermo-Systems Incorporated, Model 3045) before it is introduced into the dust chamber. The active element of the neutralizer is a 10 millicurie krypton-85 beta source. Beta rays from the krypton-85 interact with air molecules to generate both positive and negative ions. The ions become attached to the dust particles of opposite charge.

The dust chamber itself was constructed from two stainless steel stock pots. The pots are held together by three latches. An O-ring is used to provide an air-tight seal between the two pots. The chamber diameter is 14 inches and its height is 32 inches. Baffles were placed at the entrance and exit of the dust chamber to promote uniform distribution of the aerosol. The baffles are 5.75 inches in diameter, 0.015 inches thick, and are located approximately 1.5 inches away from the exit and entrance ports. The dust chamber is normally operated at a slight positive pressure with respect to the atmosphere (about 2 inches of H_2O). Effluent from the dust chamber is vented to a hood through a one-inch rubber hose.

Twelve sampling ports are located around the periphery of the dust chamber. The filter cassettes are mounted on the inside perimeter of the chamber, and sample flow rate is controlled by critical orifices which are mounted outside the chamber on a U-shaped vacuum line (see Figure 2). The sampling rate is approximately 1.7 liters per minute.

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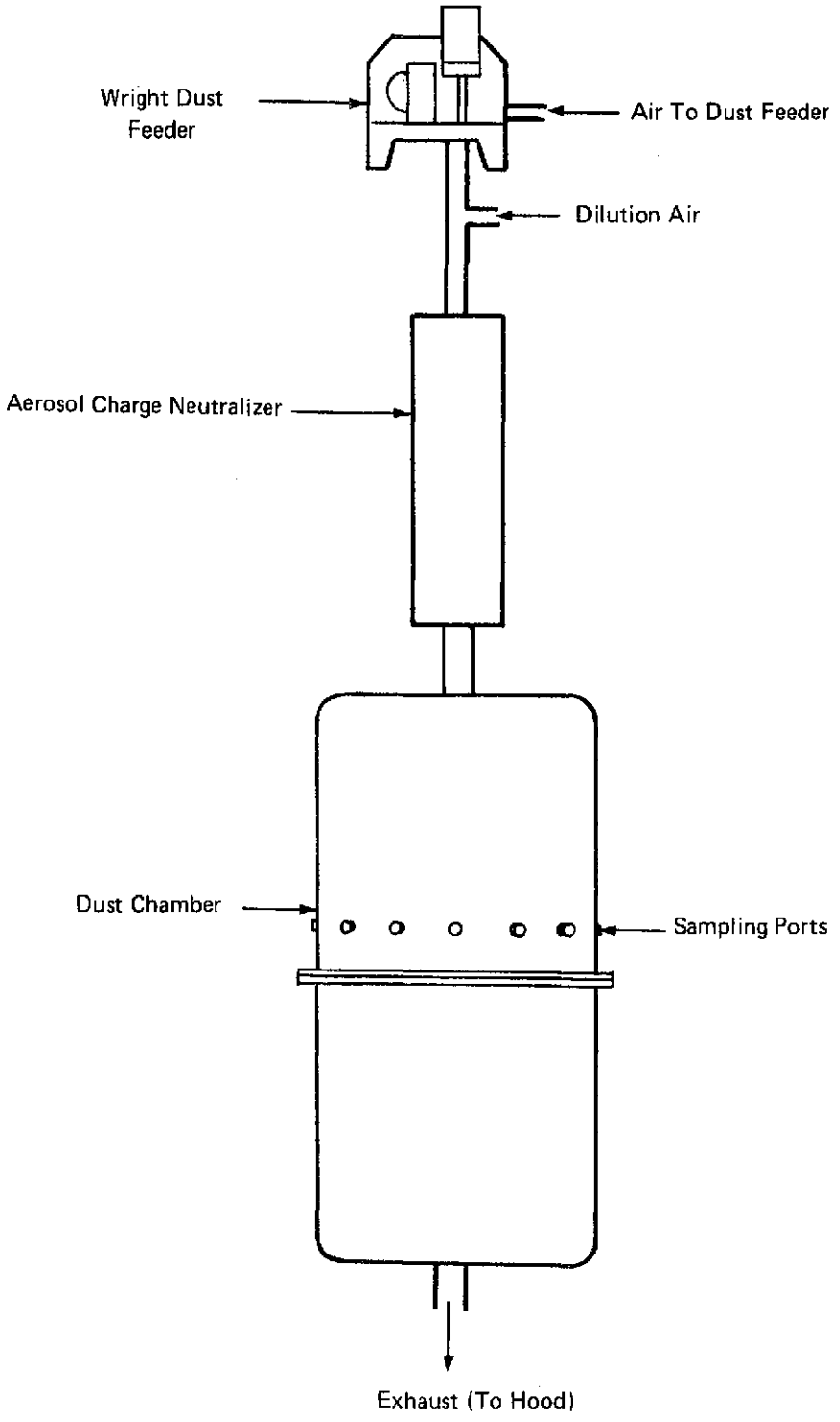

FIGURE 1 DUST GENERATION APPARATUS

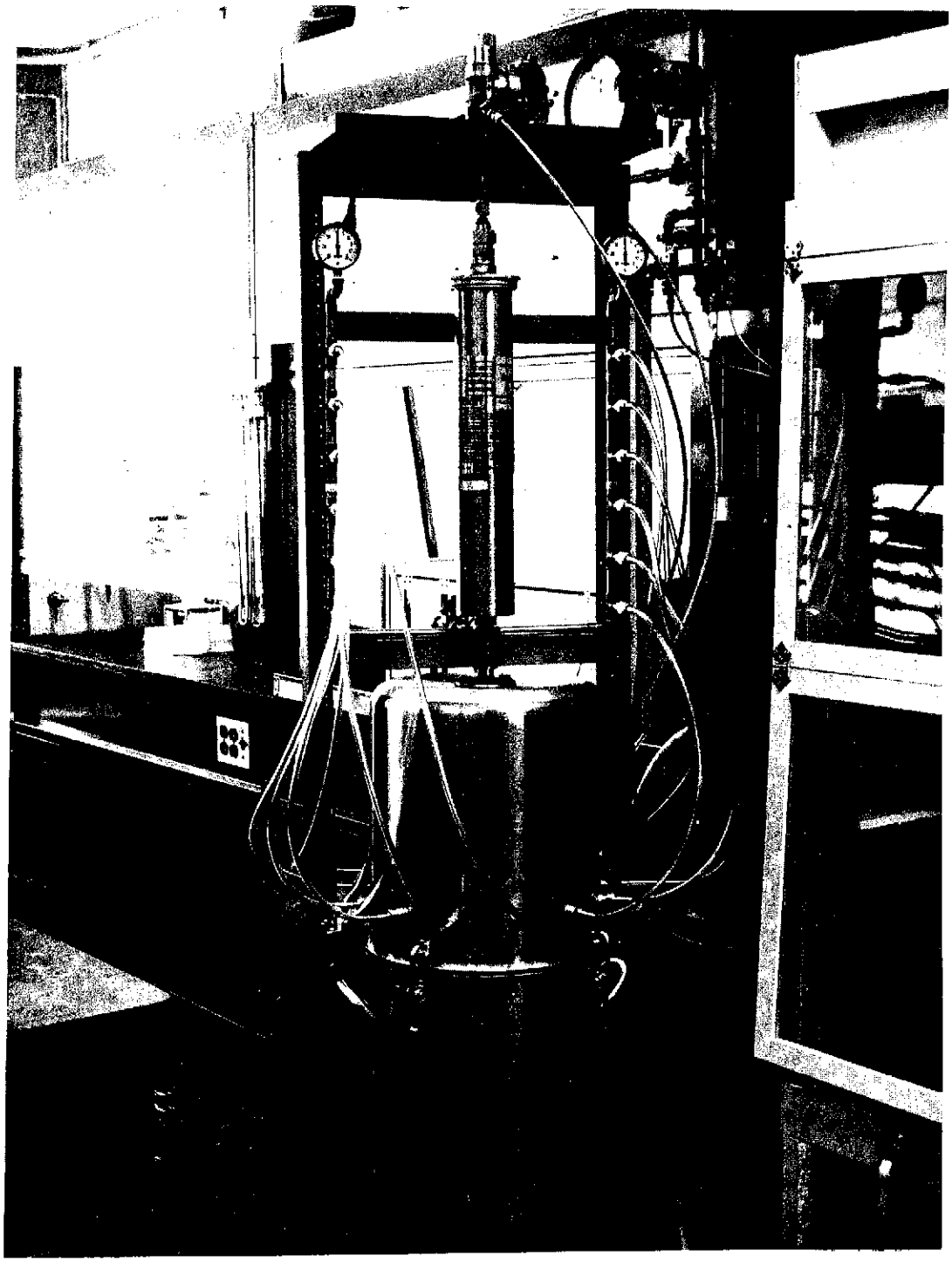

FIGURE 2 PHOTOGRAPH OF DUST GENERATION APPARATUS

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Backup Data Report

Substance: Carbon Tetrachloride, No. S314

OSHA Standard: 65 mg/cu m (T.W.A.)
160 mg/cu m (Ceiling)
1260 mg/cu m (Peak - maximum duration of 5 minutes in any 4 hours)

Chemical used for validation: Carbon Tetrachloride, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S314 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of carbon tetrachloride represented in a 15-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler, using decane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA ceiling level were generated by delivering 31.0 mg/min of carbon tetrachloride via a syringe injector to a dry air stream flowing at a rate of 0.1010 cu m/min. The three sample lines were then maintained at dilution ratios of 0.240, 0.499 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 15 minutes (17 liters). The generator concentration was also determined using M3 for calibration as described in the Propane S87 Backup Data Report. The generator concentration as determined from the total hydrocarbon data--65, 146 and 299 mg/cu m--was used as the primary basis for the generator. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold at least 15 mg of carbon tetrachloride when a test atmosphere containing 322 mg/cu m of

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carbon tetrachloride in air was sampled at 0.187 liters per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. In addition, the backup sections of the 17-liter samples collected at 1.1 liters per minute at 2X the OSHA ceiling level were also analyzed. No trace of carbon tetrachloride was found in any of the 6 backup tubes analyzed indicating that the collection efficiency is 100%.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for carbon tetrachloride as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 11.82 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for carbon tetrachloride show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0369 \qquad \overline{CV}_2 = 0.0756 \qquad \overline{CV}_T = 0.0919$$

The average recovery of the generated samples over all levels was

$$96.5 \pm 10.3\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Carbon Tetrachloride

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.268	1.200	0.946	2.378	2.132	0.897	4.75	4.59	0.966
1.268	1.202	0.948	2.378	2.066	0.869	4.75	4.71	0.992
1.268	1.339	1.056	2.378	2.147	0.903	4.75	4.65	0.979
1.268	1.325	1.045	2.378	2.316	0.974	4.75	4.77	1.004
1.268	1.283	1.012	2.378	2.197	0.924	4.75	4.62	0.973
1.268	1.238	0.976	2.378	2.223	0.935	4.75	4.60	0.968
n =		6			6			6
mean		0.997			0.917			0.980
std dev		0.0478			0.0361			0.0149
CV_1		0.0480			0.0394			0.0152

$\overline{CV}_1$ 0.0369

$\overline{CV}_{A+\overline{DE}}$ 0.0399

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Data Sheet: Carbon Tetrachloride, S314

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.145	1.145	16.88	67.8	65.0	
	1.164	1.164	16.61	70.1	65.0	
	0.901*	0.901*	16.61	54.2*	65.0	
	1.159	1.159	16.85	68.8	65.0	
	1.167	1.167	16.74	69.7	65.0	
	1.130	1.130	16.67	67.8	65.0	
			n = 5			
			mean	68.8		105.8
			std dev	1.06		
			CV_2	0.0154		
1S	2.169	2.345	16.77	139.8	146.0	
	2.089	2.258	16.86	133.9	146.0	
	2.120	2.292	17.07	134.3	146.0	
	2.199	2.377	16.91	140.6	146.0	
	1.902	2.056	16.76	122.7	146.0	
	2.116	2.288	16.77	136.4	146.0	
			n = 6			
			mean	134.6		92.2
			std dev	6.46		
			CV_2	0.0480		
2S	3.57	3.72	16.55	224.8	299.0	
	4.60	4.77	16.50	289.1	299.0	
	4.60	4.77	16.73	285.1	299.0	
	3.99	4.14	16.80	246.4	299.0	
	4.59	4.76	16.79	283.5	299.0	
	5.00	5.18	16.61	311.9	299.0	
			n = 6			
			mean	273.5		91.5
			std dev	31.8		
			CV_2	0.1163		
			$\overline{CV_2}$	0.0756		

*These values excluded from statistical analysis

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Backup Data Report

Substance: Silica, Crystalline, No. S315

OSHA Standard:

Quartz (respirable)	=	$\frac{10 \text{ mg/cu m}}{\% \text{ SiO}_2 + 2}$
Quartz (total)	=	$\frac{30 \text{ mg/cu m}}{\% \text{ SiO}_2 + 2}$
Cristobalite and Tridymite	=	1/2 the value calculated for quartz

Chemical Used for Validation: Granite Dust supplied by NIOSH, quartz content is 29.35% SiO_2 (Reference 1)*

Procedure:

The general principle of the method for crystalline silica is based on collection of the sample on silver membrane filter and determination of the crystalline (free) silica phase (quartz, cristobalite, tridymite) by X-ray diffraction analysis (direct method).

The general analysis procedure used which includes the preparation of calibration standards, performance of the analysis, and calculation of results are described in detail in NIOSH Method No. S315 (Reference 2). This method is an adaptation of the procedure described in Appendix H of Reference 3 with some modifications.

For these validation studies, the precision and accuracy of the total sampling and analytical method is based only on the analysis of the 18 generated/collected samples. Analytical samples were not prepared for the following reasons. The liquid suspension and dust dispersion methods described in Section 9.1 of NIOSH Method No. S315 are the only candidate methods for preparing analytical samples. The dust dispersion method was used for the preparation of calibration standards and is in effect also the method used for preparing the generated/collected samples. On the other hand, using the liquid suspension method to prepare analytical samples could lead to significant errors due to problems of sample preparation which are not necessarily components of field sample errors. The general coefficient of variation which has been observed to be associated with the liquid suspension method is at best 10-15% in the range of 25-50 µg free silica. This value is greater than the requisite analytical precision for this program (Reference 4).

*Reference 1, p. 174 - The free silica content is based on value reported by Talvitie for the original Granite dust sample used for this study.

The generated samples were collected on 25 mm, 1.2 micrometer pore size silver membrane filters (Selas Flotronics) via a 10 mm Dorr-Oliver cyclone; the cyclone served as a particle size separator so that only the respirable particles were collected and analyzed. The calibration standards were prepared using the dust dispersion method.

Modification

The analytical method described in Appendix H of Reference 3 was modified with respect to the data treatment aspect and the inclusion of a procedure for determination of % SiO_2 in bulk air samples. These items are addressed in the discussion section.

Discussion

The primary reference used for these validation studies was the Final Report for NIOSH Contract No. CDC-99-74-51 (Reference 3).

A. Data Treatment

The mathematical expressions used in Appendix H of Reference 3 and those ultimately recommended in NIOSH Method No. S315 are summarized in Attachment A.

The mathematical equations used in Appendix H inherently correct for X-ray absorption of standards as well as of the unknown samples. This correction factor is based on the measured relative intensities of the underlying silver membrane filter loaded with standard or samples and the clean filters. The reliability of the data based on the Appendix H method is very strongly dependent on the reproducibility of the intensity of the silver membrane filters used for standards, samples and clean filters. (Refer to Equations A-1 and A-3. In cases where the calibration standards do not require correction for X-ray absorption, Eq. A-2 could be used.)

In order to address the concern about reproducibility of intensity from silver membrane filters, a few factors were considered. Some empirical calculations were carried out in order to estimate the conditions under which a correction for standard air sample X-ray absorption could be ignored without introducing a significant error. Table 1 shows the ratio of C°/K° and the estimated % error (underestimate) for various loadings of silica standards on filters with effective areas of 2.138 sq cm (liquid suspension) and 3.80 sq cm (dust dispersion). The calculated values show that standard silica loadings (pure material) of up to 100 µg can cause only a small error (4%) for the samples prepared by dust dispersion; the errors are relatively higher for standards prepared by the liquid suspension method due to the smaller effective sample area. Table 2 shows the magnitude of the errors which can be introduced if absorption corrections for collected samples are ignored. Note that for $T_{Ag} \leq 0.90$, the error is less than 9%.

On the basis of these considerations, the original equations (designated herein as Method A in Attachment A) were simplified into a format

TABLE 1

Empirical Calculations of Estimated % Error as a Function of Silica Standard Loadings

µg SiO_2 Standard	2.138 sq cm*		3.80 sq cm*	
	-C°/K°	% Error	-C°/K°	% Error
1	0.6107	--	0.6107	--
10	0.6111	0.1	0.6109	0
50	0.6128	0.3	0.6119	0.2
100	0.6150	0.7	0.6131	0.4
200	0.6193	1.4	0.6155	0.8
500	0.6325	3.6	0.6229	2.0
1000	0.6548	7.2	0.6352	4.0

$$\frac{C^\circ}{K^\circ} = \frac{\text{Eq. A-2}}{\text{Eq. A-1}}$$

* These are standard 25-mm silver membrane filters; the difference in effective area is due to the dimensions of the cassette (dust dispersion) and the filter funnel (liquid suspension).

TABLE 2

Estimated Errors in Sample Measurement Due to Ignoring Absorption Correction

T_{Ag}	$\frac{-1.637 \ln T_{Ag}}{\left(1 - T_{Ag}^{R}\right)}$	% Error
0.99	1.008	0.8
0.95	1.043	4.3
0.90	1.089	8.9
0.80	1.194	19.4
0.50	1.672	67.2

which ignores absorption correction under certain conditions (designated as Method B. Eq. B-1 is used to calculate the K° value for standard sample loadings which can be up to 500 µg (liquid suspension) or 1000 µg (dust dispersion). For the unknown samples, the extent of sample absorption is determined based on intensities of underlying silver membrane filters (Eq. B-2) and the appropriate equation is used to determine mass of silicas depending on the observed T_{Ag} value (Eq. B-3 and Eq. B-4). In NIOSH Method No. S315, it is specifically recommended that 12 blank filters from the same lot as those used for sample collection be shipped to the laboratory to serve as control clean filters and for use in the preparation of bulk air samples. This recommendation should control the introduction of significant error due to variations in intensities of the silver membrane filter from lot to lot. The general observations under these validation studies and the earlier study (Reference 3) was that the precision of I_{Ag} values of filters from the same lot is in the order of 3-4%.

The data for the 12 calibration standards used in these validation studies are summarized in Table 3. The table includes measured values (mass, intensity of sample and of underlying silver membrane filter) and the calculated values of "old" and "new" K° and C°. The C° and the "new" K° values are comparable because both assume that no correction for absorption is required. The "new" K° value is about 5% higher than the C° value. It is highly recommended that every laboratory which performs this analysis must determine a historical average K° value. The use of a historical average will improve the accuracy of the method and can be used as a guide for evaluating the validity of a newly determined K° value.

The results of the analysis of the generated/collected samples were calculated by using the original equations (Table 4) and the revised equations (Table 5) in conjunction with the appropriate average K° value.

B. Method for % SiO_2 in Bulk Air Samples

The method tested for the determination of % SiO_2 in bulk air samples consisted of preparing samples by the liquid suspension method and sample analysis by X-ray diffraction.

Initial experimental studies under this SCP validation program were conducted by preparing a suspension of the bulk sample in isopropyl alcohol at a concentration of 20 mg Granite Dust (29.35% SiO_2) in 1 liter. Eight filter samples were prepared by filtration of 50-ml aliquots (1000 µg sample) using 0.8 micrometer pore size silver membrane filters. The data for these samples gave an average % SiO_2 found of 61.5% with poor precision, CV = 16.6%. A repeat of this experiment using the same sample stock solution for the preparation of a separate set of 4 filter samples using tared 1.2 micrometer pore size silver membrane filters gave a similar high value of 70% with equally poor precision. Of the various factors considered which may have caused

TABLE 3

Summary of Relative Magnitude of Calibration Constants ("old" K°, C°, "new" K°)

µg Quartz	I_s	I_{Ag}	-K° (old)	C°	K° (new)
206	3594	65085	4681	2880	2858
208	3746	60302	4201	2585	2769
208	3683	60799	4309	2651	2816
204	3505	60811	4442	2733	2902
180	3629	58463	3543	2239	2473
190	3829	60187	3570	2306	2474
Mean =		60941	4171	2566	2715
CV =		0.036	0.096	0.097	0.071
115	1614	59398	5330	3268	3553
103	1601	62801	5091	3119	3208
104	1600	63060	5165	3165	3241
118	1745	63397	5399	3310	3372
114	1696	59356	5025	3080	3352
118	1608	65048	6011	3685	3659
Mean =		62177	5337	3271	3398
CV =		0.037	0.067	0.068	0.052

Additional Information:

Mean I^*_{Ag} (Clean Silver Filter) = 64582

Mean I^*_M (Mica Standard) = 189540

Effective area of filter = 3.80 sq.cm.

TABLE 4

Data Sheet: Silica, Crystalline, No. S315

Sampling and Analysis*

Test Level	Found by Method A		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	34	210	0.162
	32	209	0.153
	35	212	0.165
	35	203	0.172
	37	211	0.175
	36	210	0.171
		n = 6	
		mean	0.166
		std dev	0.0081
		CV_2	0.0487
1S	94	210	0.448
	101	211	0.479
	94	207	0.454
	89	212	0.420
	85	209	0.407
	85	206	0.413
		n = 6	
		mean	0.437
		std dev	0.0281
		CV_2	0.0642
2S	177	218	0.812
	188	211	0.891
	182	214	0.850
	179	216	0.829
	191	217	0.880
	177	219	0.808
		n = 6	
		mean	0.845
		std dev	0.0349
		CV_2	0.0413
	CV_2 0.0523		

* These results are based on using average value of "old" K° and Eq. A-3 (Method A).

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TABLE 5

Data Sheet: Silica, Crystalline, No. S315

Sampling and Analysis*

Test Level	Found by Method B		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	36	210	0.171
	34	209	0.163
	37	212	0.175
	36	202	0.178
	39	211	0.185
	39	210	0.186
		n = 6	
		mean	0.176
		std dev	0.0087
		CV_2	0.0495
1S	100	210	0.476
	105	211	0.498
	100	207	0.483
	95	212	0.448
	93	209	0.445
	95	206	0.461
		n = 6	
		mean	0.468
		std dev	0.0208
		CV_2	0.0445
2S	195	218	0.894
	195	211	0.924
	198	214	0.925
	192	216	0.889
	198	217	0.912
	189	219	0.863
		n = 6	
		mean	0.901
		std dev	0.0239
		CV_2	0.0266
	CV_2 0.0414		

* These results are based on using average value of "new" K° and Eq. B-3 (Method B).

these high values, the main problem was attributed to probable agglomeration and non-uniform sample loading on the filter due to the use of more concentrated suspensions. Note that the concentration of the sample dispersions used for this study was 20 µg/ml vs 1 µg/ml for the liquid suspension studies cited in Reference 3.

Thus, another set of 3 tared, silver membrane filters (1.2 micrometer pore size) were loaded with Granite Dust bulk sample by filtration of 250 ml of a suspension containing 2.3 µg Granite Dust per ml of isopropyl alcohol. The analytical data for these samples summarized herein show that accurate results could be obtained using a less concentrated suspension.

	Method A		Method B	
µg Granite Dust	µg SiO_2	% SiO_2	µg SiO_2	% SiO_2
554	147	26.5	154	27.8
556	165	29.7	173	31.1
604	178	29.5	186	30.8
	Average	28.6	---	29.9
	CV	0.063	---	0.062

The average % SiO_2 found using either Method A or Method B to calculate results is in excellent agreement with the 29.35% SiO_2 value found by twelve analysts using the colorimetric method for crystalline silica (Reference 1). The procedure recommended in Section 8.5 of NIOSH Method No. S315 is based on these findings.

A recommendation for the collection of bulk air sample is also included in NIOSH Method No. S315 and in the Sampling Data Sheet No. S315. To collect a respirable bulk air sample, the use of a 1-inch HASL cyclone is recommended. This choice is based on the article of Lippman and Chan (Reference 5) which shows that the particle size acceptance curve of the 1-inch HASL cyclone agrees well with the ACGIH respirable particle size criteria at a sampling rate of 75 liters per minute. The cyclone is connected in series to a Fluoropore Filter and Gast 1022 vacuum pump.

C. Description of Granite Dust Sample Used

The Granite Dust sample used for these studies was supplied by NIOSH for the previous program (Reference 3) and is from the same batch of Granite Dust reported by Talvitie (Reference 1) to contain 29.35% SiO_2 as quartz, with a standard deviation of 0.56. The 29.35% SiO_2 reported by Talvitie is based on the data obtained by 12 analysts. The sample,

as received from NIOSH, was 200 mesh screened and required further particle size reduction by wet milling for 10 days. This handling procedure produced particles less than 10 μm in size by optical microscopy determination (Reference 3, p. A-1). The conversion of the 200-mesh particles to the 10-micron particles did not alter the % SiO_2 composition of the Granite Dust sample. This is supported by the data summarized in Section B of this Discussion Section and also by the data on six samples generated and collected via the dust dispersion route. These data are summarized in Table 6. The average % SiO_2 found was 29.0% by Method A calculations vs 30.9% by Method B calculations. These values are in excellent agreement with the value reported by Talvitie--29.35% SiO_2.

Generation

The basic system used to generate crystalline silica atmospheres using samples of Granite Dust (29.35% SiO_2) is described in detail in Attachment B.

For the generation of the desired crystalline silica test atmospheres, Granite Dust was loaded into the dust container in a series of roughly one gram quantities. After each addition, the powder was spread out to produce a layer of uniform thickness, and it was then compressed lightly (about 300 lbs) with a laboratory press. The concentration of the crystalline silica in the chamber was controlled by proper adjustment of the dust holder advance rate, and the three test level concentrations were generated independently.

The OSHA standard for respirable quartz containing 29.35% SiO_2 was calculated to be 0.319 mg/cu m. Test atmospheres were therefore generated using this value as the basis for producing the 0.5X, 1X and 2X OSHA standard test levels. To produce these low test concentrations, the dilution air flow was regulated at 300, 200 and 100 liters/per minute coupled with the appropriate dust holder advance rate to produce the respective 0.5X, 1X and 2X OSHA standard test levels.

Although 12 samples can be collected simultaneously, only six samples for each test level were collected and analyzed. Samples were collected at 1.7 liters per minute for 120 minutes (210 liters). The atmospheric temperature and pressure during these generation/collection experiments varied within the respective range of 24-28°C and 760-764 mm Hg.

A Dorr-Oliver cyclone was used before each filter. Thus only the particles in the respirable size range were collected and tested. Under the conditions of these experimental tests, the fraction passing the size-selector has the following characteristics (Reference 6):

TABLE 6

Free Silica (% SiO_2) Content of Granite Dust

A. Data Obtained by Method A Calculation

µg SiO_2 Found[1]	Total µg of Sample Collected[2]	% SiO_2
177	619	28.6
188	646	29.1
182	650	28.0
179	593	30.2
191	625	30.6
177	646	27.4
	Mean	29.0
	CV	0.043

B. Data Obtained by Method B Calculation

µg SiO_2 Found[1]	Total µg of Sample Collected[2]	% SiO_2
195	619	31.5
195	646	30.2
198	650	30.5
192	593	32.4
198	625	31.7
189	646	29.3
	Mean	30.9
	CV	0.037

[1] As determined by X-ray diffraction analysis.

[2] As determined based on weight difference of silver membrane filter before and after sample collection.

Aerodynamic Diameter (μm) (unit density sphere)	% passing selector
≤ 2	90
2.5	75
3.5	50
5.0	25
10	0

The data for the set of 18 samples are shown in Table 4 where Method A was used to calculate μg Found and in Table 5 (for the same samples) where Method B was used.

Collection Efficiency

A set of 6 generated samples collected on 25-mm, 1.2 micrometer pore size silver membrane filters was used for these studies. The front and backup filters were arranged in the 25-mm filter cassette holder such that the two filters were mounted back to back and in contact with each other; the filters were supported by a 25-mm, stainless steel screen. The average collection efficiency was found to be 100% for the test atmospheres containing 0.846 mg/cu m for a 210 liter sample collected at 1.7 liter per minute (Table 7).

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Attachment C and the data in Tables 4 and 5. The precision is expressed in terms of the coefficients of variation for the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below for Method A and Method B data treatment.

Based on Method A:

$\overline{CV}_2 = 0.0523$ $\overline{CV}_T = 0.072$

Based on Method B:

$\overline{CV}_2 = 0.0414$ $\overline{CV}_T = 0.065$

The accuracy of the method can be estimated based on the data for the six samples at the 2S test level. These samples were collected on tared silver membrane filters to allow determination of sample weight collected. The data for these samples are summarized in Table 6 expressed in % SiO_2 and in Tables 4 and 5 (2S level) expressed in mg/cu m.

TABLE 7

Collection Efficiency: Silica, Crystalline (Respirable)

Generator Concentration: 0.846 mg/cu m
Sample Volume: 200 liters at 1.7 liters per minute

Front	Backup	Total	% Collected on Front
176.8	ND	176.8	100.0
174.0	ND	174.0	100.0
176.9	ND	176.9	100.0
171.4	ND	171.4	100.0
176.4	ND	176.4	100.0
168.4	ND	168.4	100.0

Average Collection Efficiency . . . 100.0%

ND = Not Detectable; the detection limit was 5 µg.

TABLE 8

DETERMINATION OF ACCURACY

	mg/cu m Taken	mg/cu m Found	
		Method A	Method B
	0.828	0.812	0.894
	0.899	0.891	0.924
	0.891	0.850	0.925
	0.806	0.829	0.889
	0.845	0.880	0.912
	0.865	0.808	0.863
Average =	0.856	0.845	0.901
CV =	0.036	0.041	0.027
$\frac{\text{Found}}{\text{Taken}} \times 100 =$		98.7%	105.3%

An estimate of the mg/cu m taken can be determined based on tared sample weight, the reported free silica content (29.35%) and the sample volume. These values can be compared with the mg/cu m found to estimate the accuracy of the method. This exercise was carried out only for the 2S test level because of uncertainties associated with weight determinations at the 1S and 0.5S test levels. These values are summarized in Table 8 for the case in which Method A and Method B data treatment was used.

References

1. Talvitie, N.A., "Determination of Free Silica: Gravimetric and Spectrophotometric procedures applicable to Air-borne and Settled Dust," Am. Ind. Hyg. Assoc. J., 25, 169-178 (1964).

2. NIOSH Method No. S315, "Silica, Crystalline," prepared under NIOSH Contract No. CDC-99-74-45, Validation Date - 1/30/76, report submitted in October, 1976.

3. Peters, E.T., "Evaluation of the NIOSH X-ray Diffraction Method for the Determination of Free Silica in Respirable Dust," Final Report to NIOSH under Contract No. CDC-99-74-51, May, 1976.

4. Kenneth A. Busch Memoranda to Deputy Director, DLCD, on the subject "Statistical Protocol for Analysis of Data from Contract No. CDC-99-74-45," dated 1/16/75, 11/8/74.

5. Lippmann, M. and Chan, T.L., "Calibration of Dual-Inlet Cyclones for 'Respirable' Mass Sampling," Am. Ind. Hyg. Assoc. J., 35, 189-200 (1974).

6. Publication of Am. Conference of Governmental Industrial Hygienists, "Threshold Limit Values for Chemical Substances and Physical Agents in The Workroom Environment with Intended Changes," 1976, p. 33.

7. Leroux, J., Davey, A. and Paillard, A., "Proposed Standard Methodology for the Evaluation of Silicosis Hazards," Amer. Ind. Hyg. Assoc. J., 34, 409 (1973).

Attachment A

Summary of Mathematical Equations

Method A: Original Equations used (from Reference 3)

$$K^\circ = \frac{I_{Ag}^\circ \cdot \sin\theta_{Ag} \left[\exp\left(\frac{-2(\mu/\rho)_S \, W_S^\circ}{A^\circ \sin\theta_S} \right) - 1 \right]}{C \cdot I_S^\circ \cdot 2(\mu/\rho)_S} \qquad \text{Eq. A-1}$$

$$C^\circ = \frac{I_{Ag}^\circ \cdot W_S^\circ}{C \cdot I_S^\circ \cdot A^\circ} \qquad \text{Eq. A-2}$$

where:

K° = calibration constant taking into account X-ray absorption of standard samples

C° = calibration constant where an X-ray absorption correction can be ignored

I_{Ag}° = intensity of the underlying silver filter

θ_{Ag} = diffraction angle for silver

θ_S = diffraction angle for the crystalline (free) silica line and polymorph

W_S° = mass of crystalline (free) silica standard in µg

I_S° = intensity of the crystalline (free) silica standard

$(\mu/\rho)_S$ = absorption coefficient for silica (34.8 for CuK_α radiation)

A° = effective area of filter (sq cm)

and $C = I_{Ag}^*/I_M^*$

where:

I_{Ag}^* = average intensity of clean silver filters

I_M^* = average intensity of the mica calibration standard as determined in Section 9.3 (Reference 3)

$$W_S = \frac{K^\circ \cdot I_S \cdot A \cdot \ln T_{Ag}}{I_M \left(1-T_{Ag}^{\,R}\right)} \qquad \text{Eq. A-3}$$

where:

W_S = sample mass of crystalling (free) silica phase in micrograms

I_M = intensity of the mica instrument calibration standard

A = effective area of the sample collection filter (sq cm)

$T_{Ag} = \frac{I_{Ag}}{C\ I_M}$ and $R = \frac{\sin\theta_{Ag}}{\sin\theta_S}$

The other symbols are as identified in preceding portions of Section A.

Method B: Alternative Equations Recommended in NIOSH Method No. S313

$$K^\circ = \frac{I_M^*}{i} \sum_{\circ}^{i} \frac{W_S^\circ}{A^\circ\ I_S^\circ} \qquad \text{Eq. B-1}$$

It is recommended that each laboratory performing this analysis should determine a historical average K° value.

where:

K° = calibration constant

I_S° = intensity of the crystalline (free) silica standard

W_S° = mass of crystalline (free) silica standard in µg

A° = effective area of filter (sq cm)

i = number of standard filters in set

I_M^* = average intensity of the mica calibration sample as determined in Section 9.4.

$$T_{Ag} = \frac{I_{Ag}}{C\ I_M} \qquad \text{Eq. B-2}$$

where:

I_{Ag} = intensity of the underlying silver filter

I_M = intensity of the mica instrument calibration standard

$C = I_{Ag}^*/I_M^*$

where:

I_{Ag}^* = average intensity of clean silver filters as determined in Section 9.4

I_M^* = average intensity of the mica calibration standard as determined in Section 9.3

For $T_{Ag} \geq 0.90$:

$$W_S = \frac{K^\circ \cdot I_S \cdot A}{I_M} \qquad \text{Eq. B-3}$$

For $T_{Ag} < 0.90$:

$$W_S = \frac{-R\,K^\circ \cdot I_S \cdot A \cdot \ln T_{Ag}}{I_M \left(1-T_{Ag}^{\,R}\right)} \qquad \text{Eq. B-4}$$

where:

W_S = mass of crystalline (free) silica phase in the sample in µg

K° = calibration constant as in Equation B-1

I_S = intensity of crystalline (free) silica phase

A = effective area of the sample collection filter (sq cm)

I_M = intensity of the mica instrument calibration standard

$$R = \frac{\sin\theta_{Ag}}{\sin\theta_S}$$

where:

θ_{Ag} = diffraction angle for silver

θ_S = diffraction angle for the crystalline (free) silica line and polymorph

Attachment B

Description of Dust Atmosphere Generation Apparatus

The basic elements of the system used to generate the dust test atmospheres are shown in Figures 1 and 2. The system consists of a Wright Dust Feeder, an aerosol charge neutralizer, and an 80-liter stainless dust chamber.

Dust samples to be dispersed in the apparatus are compressed into a container which is attached to the Wright Dust Feeder. In operation, the container and the dust compact are slowly rotated and driven against a stationary scraper blade by an electrically-operated mechanism. The blade continuously removes dust from the compact surface at a uniform rate. Compressed air enters the container and entrains the dust particles. The dust holder advance rate may be varied by changing the gears in the drive mechanism to provide a wide range of dust concentrations.

A short distance downstream of the dust feeder there is an auxiliary port for introducing additional air for further dilution of the dust cloud. Normally, a flow of 30 liters per minute is passed through the dust feeder itself, and dilution air is added at the rate of 70 liters per minute. Air flow rates are read from calibrated rotameters. Compressed air is supplied to the apparatus from the house compressed air system. This air is dried by passing it through a silica gel bed and then through a high efficiency fibrous filter and a membrane filter to remove particulate matter.

Since dust particles may accumulate electric charges in the dispersal process, the dispersed dust is passed through a charge neutralizer (Thermo-Systems Incorporated, Model 3045) before it is introduced into the dust chamber. The active element of the neutralizer is a 10 millicurie krypton-85 beta source. Beta rays from the krypton-85 interact with air molecules to generate both positive and negative ions. The ions become attached to the dust particles of opposite charge.

The dust chamber itself was constructed from two stainless steel stock pots. The pots are held together by three latches. An O-ring is used to provide an air-tight seal between the two pots. The chamber diameter is 14 inches and its height is 32 inches. Baffles were placed at the entrance and exit of the dust chamber to promote uniform distribution of the aerosol. The baffles are 5.75 inches in diameter, 0.015 inches thick, and are located approximately 1.5 inches away from the exit and entrance ports. The dust chamber is normally operated at a slight positive pressure with respect to the atmosphere (about 2 inches of H_2O). Effluent from the dust chamber is vented to a hood through a one-inch rubber hose.

Twelve sampling ports are located around the periphery of the dust chamber. The filter cassettes are mounted on the inside perimeter of the chamber, and sample flow rate is controlled by critical orifices which are mounted outside the chamber on a U-shaped vacuum line (see Figure 2). The sampling rate is approximately 1.7 liters per minute.

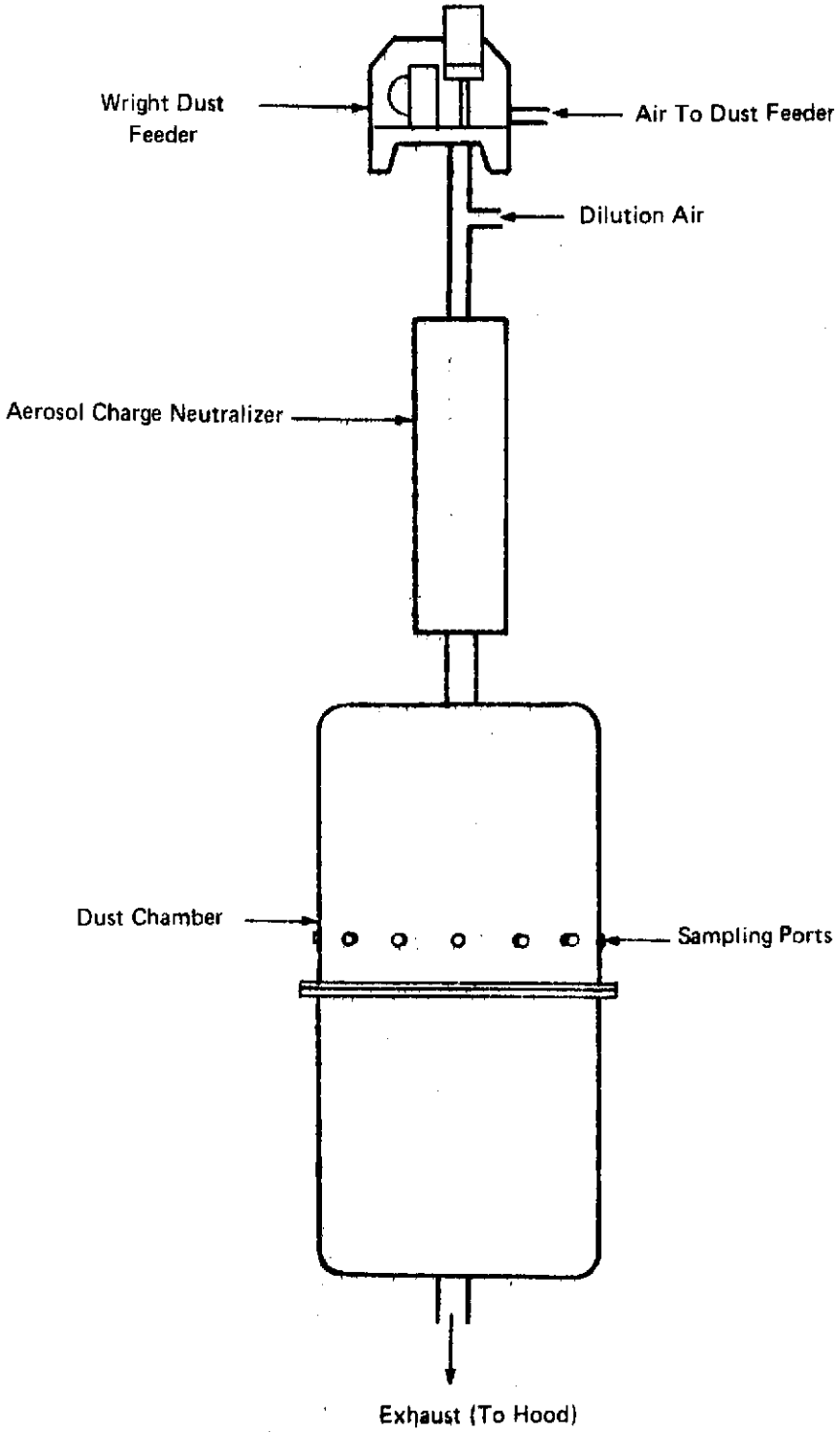

FIGURE 1 DUST GENERATION APPARATUS

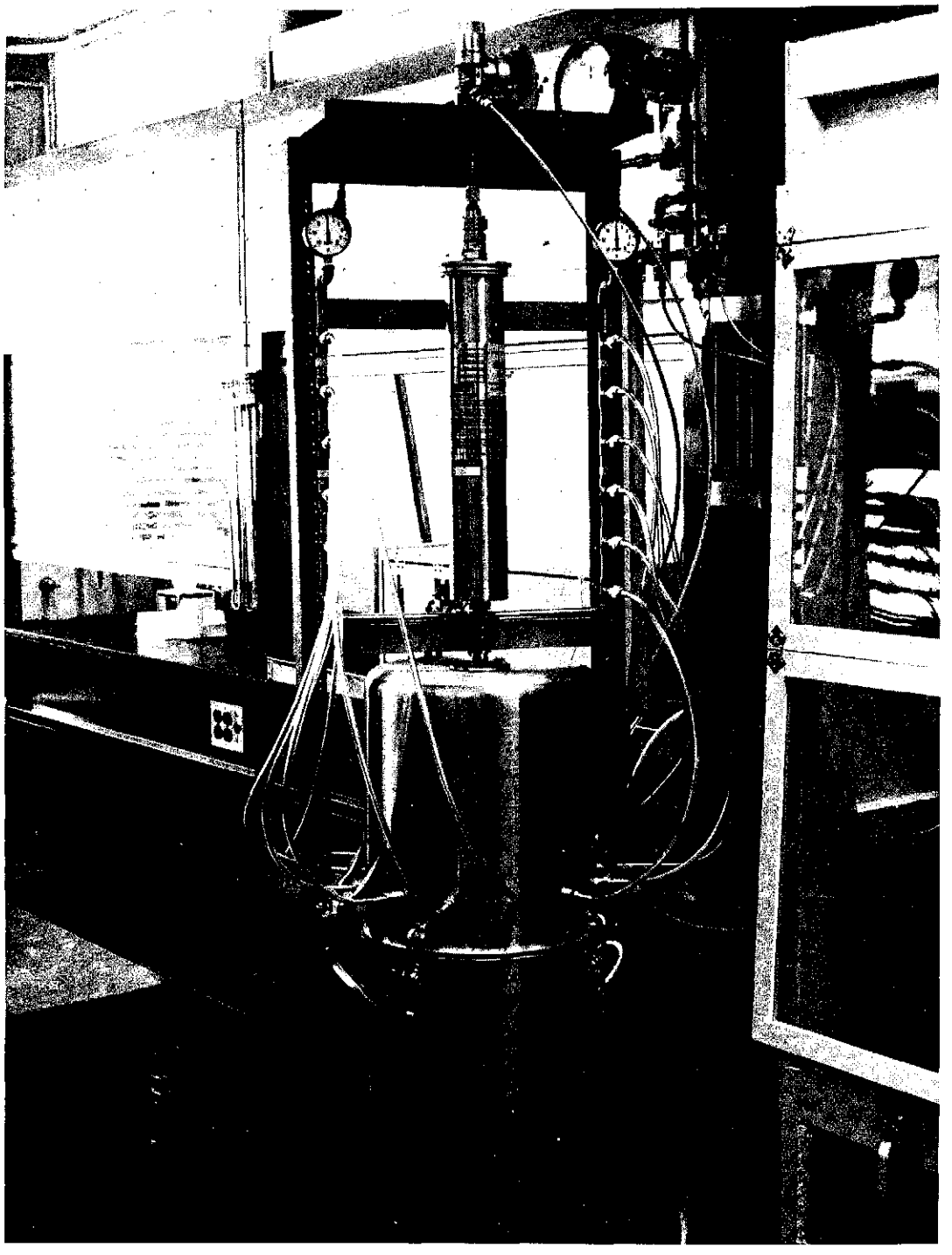

FIGURE 2 PHOTOGRAPH OF DUST GENERATION APPARATUS

Attachment C

SUMMARY OF STATISTICAL TERMS AND FORMULAE

The statistical analysis employed in this program has been provided by NIOSH. The evaluation of the limits and guidelines are discussed in a series of memoranda from Busch (Reference A). Some key terms, statistical formula, acceptable limits and statistical tests which have been used in these reports are noted and summarized herein.

Mean - Arithmetic mean or average, defined as the sum of all the observations divided by the number of observations (n).

Standard deviation - defined as the positive square root of the variance which is defined as the sum of squares of the deviations of the observations from the mean ($\bar{x}$) divided by one less than the total number of observations (n-1).

$$\text{std dev} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}$$

CV - Coefficient of Variation or Relative Standard Deviation, defined as the standard deviation divided by the mean.

$$CV = \frac{\text{std dev}}{\text{mean}}$$

CV_1 - Coefficient of Variation for the six analytical samples at each of the 0.5, 1, and 2X OSHA standard level.

CV_2 - Coefficient of Variation for the six generated samples at each of the 0.5, 1 and 2X OSHA standard level.

$\overline{CV}$ - Pooled Coefficient of Variation; in this program, the value is derived from the coefficients of variation obtained from the analysis of 6 samples at each of the three test levels - 0.5, 1 and 2X OSHA standard level. The mathematical equation is expressed as:

$$\overline{CV} = \sqrt{\frac{\sum_{i=1}^{n} f_i \, (CV_i)^2}{f}}$$

where:

f_i = degrees of freedom, equal to number of observations minus one, at the i^{th} level.

CV_i = Coefficient of Variation of the observations at the i^{th} level

$$f = \sum_{i=1}^{n} f_i$$

$\overline{CV}_1$ - Pooled Coefficient of Variation calculated as above based on data for the 18 analytical samples

$\overline{CV}_{A+\overline{DE}}$ - This is a derived correction to include error due to the use of the desorption efficiency factor which is an average of 6 values.

$$\overline{CV}_{A+\overline{DE}} = \overline{CV}_1 \sqrt{7/6} = 1.0801 \ \overline{CV}_1$$

$\overline{CV}_{A+\overline{AMR}}$ - This is a correction factor analogous to the desorption efficiency factor noted above except that this notation is used where the factor is associated with analytical method recovery (AMR).

$$\overline{CV}_{A+\overline{AMR}} = 1.0801 \ \overline{CV}_1$$

$\overline{CV}_2$ - Pooled Coefficient of Variation based on the data for the 18 generated samples.

$\overline{CV}_S$ - Coefficient of Variation of the sample collection, the value is dependent on the data from the 18 analytical and 18 generated samples.

$$\overline{CV}_S = \sqrt{\left(\overline{CV}_2\right)^2 - \left(\overline{CV}_1\right)^2}$$

$\overline{CV}_P$ - Coefficient of Variation due to the pump error, assumed to be equal to 0.05.

$\overline{CV}_T$ - Coefficient of Variation of total procedure which consists of the composite variations in sampling and analysis, desorption efficiency, and the pump error.

$$\overline{CV}_T = \sqrt{\left(\overline{CV}_S\right)^2 + \left(\overline{CV}_{A+\overline{DE}}\right)^2 + \left(\overline{CV}_P\right)^2}$$

or:

$$\overline{CV}_T = \sqrt{\left(\overline{CV}_2\right)^2 - \left(\overline{CV}_1\right)^2 + 1.1667 \left(\overline{CV}_1\right)^2 + \left(0.05\right)^2}$$

Grubb's Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

$$B_1' = \frac{x - \bar{x}}{s} \text{ or } \left(\frac{\bar{x} - x}{s}\right)$$

where:

x = observation being tested

$\bar{x}$ = mean of all observations

s = standard deviation based on n degrees of freedom.

For any 6 observations, a value can be rejected if $B_1' \geq 2.130$. The B_1' limit is based on a 1% significance level (i.e., a B_1' value calculated from the data can be expected to exceed 2.13 only 1% of the time if the observation is a legitimate one conforming to the underlying theory).

Bartlett's Test for Homogeneity of Variances

This test is applied in order to test the feasibility of "pooling the Coefficients of Variation" for any set of 18 generated samples (i.e., 6 at each of the 0.5, 1 and 2X OSHA standard level). The following equation for chi squared, with n-1 degrees of freedom, was used:

$$\text{Chi Squared} = \frac{f \ln \left(\overline{CV}_2\right)^2 - \sum_{i=1}^{n} f_i \ln \left(\overline{CV}_{2i}\right)^2}{1 + \frac{1}{3(k-1)}\left[\left(\sum_{i=1}^{n} \frac{1}{f_i}\right) - \frac{1}{f}\right]}$$

where:

$\overline{CV}_2$ = Pooled Coefficient of Variation of 18 generated samples.

$\overline{CV}_{2i}$ = Coefficient of Variation of 6 generated samples at the i^{th} level.

f_i = Degrees of freedom associated with $(CV_{2i})^2$ and equal to number of observations at the i^{th} level minus one.

i = 1, 2, 3..... n

$f = \sum_{i=1}^{n} f_i$

k = number of variances being tested; in this program k = 3.

In order to pass Bartlett's test at the 1% significance level, chi squared must be less than or equal to 9.21 when k = 3.

Reference

A. Kenneth A. Busch Memoranda to Deputy Director, DLCD, on the subject "Statistical Protocol for Analysis of Data from Contract No. CDC-99-74-45", dated 1/16/75, 11/8/74.

Backup Data Report

Substance:	Chromic Acid and Chromates, No. S317
OSHA Standard:	0.1 mg/cu m (as CrO_3) - Ceiling
Chemicals Used for Validation:	Chromium trioxide, J. T. Baker Sodium dichromate, Mallinckrodt

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of chromic acid and chromates in air is described in NIOSH Method No. S317, which has been adapted from P&CAM 169. The reliability of the analytical method was tested at sample concentrations equal to that present in a 22.5-liter sample at approximately 0.5, 1, and 2 times the OSHA standard level. Appropriate aliquots of a 100 ppm Cr(VI) standard were added to 37-mm/5 micron polyvinyl chloride filters. Chromium (VI) was extracted from the filters with 0.25 M sulfuric acid. Hexavalent chromium is analyzed by reaction with a solution of diphenylcarbazide. The absorbance of the resulting colored solution is determined spectrophotometrically at 540 nm.

Modifications

There were two modifications made to P&CAM 169.

1. The final solution volume, prior to analysis, was changed from 15 to 20 ml.

2. A 5-cm path cell is used instead of a 2-cm cuvette.

Generation

Samples of chromic acid in air were generated by the procedure described in Reference No. 1. A 0.5% solution of chromic acid in water was used in the aspiration system. To generate the three levels of chromic acid, it was necessary to vary the pressure across the aspirator from 4.5 psig to 6.0 psig. This pressure range gave particles with a median diameter of 1.5 micron. This was determined by preparation of an ammonia fluorescein solution in water which was 0.5% weight/volume. The ammonium fluorescein was aspirated at 4.5, 5.0, and 6.0 psig in separate experiments. The aerosol droplets were spray-dried in air and the resulting particulate was collected on 0.2-micron Nuclepore filters. Microscopic examination of the filters showed a mean particle size of approximately 1.5 micron.

Prior to sample collection, it was necessary to determine the amount of dilution air needed to dilute the aspirator output to produce the three desired concentration levels (0.5X, 1X, and 2X the OSHA standard level). This was necessary, because simultaneous monitoring of the generator output is not possible.

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Samples were collected and analyzed to monitor the concentration in the sampling chamber prior to collection of the 2X level samples. When the correct amount of dilution air was added to give approximately the 2X level, six samples were taken.

The output of the aspirator at 6.0 psig was diluted with air at 13.6 liters/minute to obtain approximately the 2X level. An aspirator output of 5 psig was diluted with air at 273 liters/minute to obtain approximately the 1X level. The 0.5X level was obtained by dilution of the aspirator output at 4.5 psig, with 200 liters/minute of air. Samples were collected for 15 minutes at a flow rate of 1.5 liters/min.

Collection Efficiency

Collection efficiency was determined by measuring the amount of chromic acid collected on each of two filters mounted in series in direct contact with each other. The collection efficiency of the filter was found to be 0.945 $\pm$ 0.035. The collection efficiency experiment was done at a generated concentration of 0.192 mg/cu m. The results are given in the following table:

mg/cu m in first filter	mg/cu m in backup filter	Total mg/cu m	Collection Efficiency
0.183	0.002	0.185	0.989
0.193	0.017	0.210	0.919
0.185	0.019	0.204	0.907
0.170	0.009	0.179	0.950
0.176	0.003	0.179	0.983
0.180	0.015	0.195	0.923
		mean	0.945
		std dev	0.035
		CV	0.037

Discussion

A time study at the 1X OSHA standard level was conducted. Four filters were spiked with a known amount of hexavalent chromium and stored for a period of seven days in screw cap bottles. After seven days, the filters were extracted according to NIOSH Method No. S317. The results of the time study are given in the following table:

µg taken	µg found	A.M.R.
1.212	1.200	0.990
1.212	1.100	0.908
1.212	1.110	0.916
1.204	1.230	1.022
	mean	0.959
	std dev	0.056
	CV	0.059

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From the above results, hexavalent chromium is stable on PVC filters for a period of seven days.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.018$ $\overline{CV}_2 = 0.067$ $\overline{CV}_T = 0.084$

Data Sheet: Chromic Acid and Chromates S317

Analysis

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
0.600	0.620	1.033	1.212	1.250	1.031	2.323	2.300	0.990
0.600	0.610	1.017	1.204	1.250	1.038	2.323	2.320	0.999
0.600	0.600	1.000	1.204	1.230	1.022	2.307	2.340	1.014
0.600	0.605	1.008	1.212	1.250	1.031	2.307	2.400	1.040
0.600	0.620	1.033	1.212	1.240	1.023	2.323	2.400	1.033
0.600	0.610	1.017	Sample was lost.			2.323	2.250	0.969
n =		6			5			6
mean		1.018			1.029			1.008
std dev		0.013			0.007			0.027
CV_1		0.013			0.007			0.027

$\overline{CV}_1$ 0.018

$\overline{CV}_{A+\overline{AMR}}$ 0.019

Based on these results, no analytical method recovery correction is necessary.

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Data Sheet: Chromic Acid and Chromates S317

Sampling and Analysis

Test Level		Found			
		µg	Liters	mg/cu m*	Corrected mg/cu m**
0.5S		1.173	22.71	0.0517	0.0547
		1.077	22.47	0.0479	0.0507
		1.173	21.95	0.0534	0.0565
		1.192	22.47	0.0530	0.0561
		1.000	22.50	0.0444	0.0470
		0.962	21.89	0.0439	0.0465
			n = 6		
			mean		0.0520
			std dev		0.0045
			CV_2		0.087
1S		2.019	22.71	0.0889	0.0941
		1.981	22.47	0.0882	0.0933
		2.019	21.95	0.0920	0.0974
		1.981	22.47	0.0882	0.0933
		2.154	22.50	0.0957	0.1013
		1.923	21.89	0.0878	0.0929
			n = 6		
			mean		0.0954
			std dev		0.0033
			CV_2		0.035
2S		4.06	21.71	0.187	0.198
		4.75	22.47	0.211	0.223
		4.50	21.95	0.205	0.217
		4.04	22.47	0.180	0.190
		4.06	22.50	0.180	0.190
		4.31	21.89	0.197	0.208
			n = 6		
			mean		0.204
			std dev		0.014
$\overline{CV}_2$	0.067		CV_2		0.069

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

** Corrected for collection efficiency using a collection efficiency of 0.945.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance:	Xylene (Xylol), No. S318
OSHA Standard:	100 ppm (435 mg/cu m)
Chemical Used for Validation:	Xylene Mallinckrodt

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of xylene in air is described in NIOSH Method S318, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2X, 1X, and 0.5X the OSHA standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of xylene to represent 12-liter air samples. Samples of xylene in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of xylene in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 60 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined using a total hydrocarbon analyzer which was calibrated with bag standards. The total hydrocarbon analyzer was also used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were no major modifications to P&CAM 127.

Generation

Samples of xylene in air were generated by the procedure described in Reference No. 1 with a two-piece vapor generator and a dilution system. The generator conditions used are given below:

Nitrogen flow rate:	833 ml/min at 24°C
Dilution air flow rate:	38.7 liters/min at 24°C

The concentrations in the 2X, 1X, and 0.5X sampling chambers were determined with a total hydrocarbon analyzer standardized with bag standards.

The recovery of the 0.5X generated samples were lower than expected. A second generation at the 0.5X level was conducted and found to be satisfactory.

Samples were collected for 60 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test. Breakthrough, 5% of the generated concentration of 810 mg/cu m in the effluent was observed after 172.6 minutes of sampling at a rate of 0.20 liter per minute. The test was continued until 16% of the 2X level was exceeded at the pump effluent. Sampling was discontinued after 3.11 hours of sampling.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.010 \qquad \overline{CV}_2 = 0.033 \qquad \overline{CV}_T = 0.060$

The average recovery at the OSHA standard level was 97.9%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Xylene S318

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
2.604	2.541	0.976	5.21	5.15	0.988	10.42	10.21	0.980
2.604	2.595	0.997	5.21	5.15	0.988	10.42	10.34	0.992
2.604	2.543	0.977	5.21	5.24	1.006	10.42	10.38	0.996
2.604	2.606	1.001	5.21	5.12	0.983	10.42	10.26	0.985
2.604	2.575	0.989	5.21	5.09	0.977	10.42	10.31	0.989
2.604	2.610	1.002	5.21	5.14	0.987	10.42	10.31	0.989
n =		6			6			6
mean		0.990			0.988			0.988
std dev		0.012			0.010			0.006
CV_1		0.012			0.010			0.006

The equation D.E. = $0.989 - e^{-10.68 \text{ X mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use fo this equation is given in Reference No. 4.

Data Sheet: Xylene S318

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr. mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	2.740	2.770	11.40	243.0	218	
	2.684	2.714	11.34	239.3	218	
	2.462	2.489	11.04	225.4	218	
	2.558	2.586	12.00	215.5	218	
	2.471	2.498	11.28	221.4	218	
	2.694	2.724	12.00	227.0	218	
			n = 6			
			mean	228.6		104.9
			std dev	10.6		
			CV_2	0.046		
1S	4.37	4.41	10.47	421	435	
	4.27	4.32	10.53	410	435	
	4.49	4.54	10.39	437	435	
	4.26	4.31	10.23	421	435	
	4.52	4.57	10.62	430	435	
	4.72	4.77	10.98	434	435	
			n = 6			
			mean	426		97.9
			std dev	10		
			CV_2	0.023		
2S	10.13	10.24	12.06	849	870	
	9.76	9.87	11.28	875	870	
	9.96	10.07	11.49	876	870	
	9.42	9.52	10.74	886	870	
	10.08	10.19	11.25	906	870	
	Sample was lost due to malfunctioning orifice.					
			n = 5			
			mean	878		100.9
			std dev	21		
$\overline{CV_2}$ 0.033			CV_2	0.024		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Chromium, Soluble Chromic and Chromous Salts as Cr, No. S323

OSHA Standard: 0.5 mg/cu m

Chemical Used for Validation: Potassium Dichromate Mallinkrodt

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of soluble chromic and chromous salts in air is described in NIOSH Method S323, which was adapted from P&CAM 173. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 90-liter sample at 0.5, 1, and 2 times the OSHA standard. Appropriate aliquots (20, 40, and 80 microliters) of an aqueous 1.13 microgram/microliter potassium dichromate solution were added to 37-mm/0.8-micron type AA MCEF filters. The filters were digested in concentrated nitric acid to destroy the filters and any other organic material. The digested sample was then dissolved in 1 ml concentrated nitric acid and diluted to 20 ml with deionized water prior to AA analysis. Analyses were done on a Varian Techtron AA6 atomic absorption spectrophotometer. The absorbance, measured at 357.9 nm, was used as a measure of the chromium concentration in the sample. This procedure was used for the analysis of 18 generated samples, six at each of the OSHA standard levels. Details of the analytical procedure may be found in Section 8.4 of the NIOSH Method No. S323. Details of the generation of the analyte at three concentration levels of approximately 0.5, 1, and 2 times the OSHA standard are given below.

Modifications

There were no major modifications made to P&CAM 173.

Generation

Samples of inorganic chromium particulate were generated by the procedure described in Reference 1. A 0.5% aqueous solution of potassium dichromate was used in the aspiration system. A pressure drop of 8 psi across the aspirator tip was used in the generation of the aerosol. This pressure gave particles with a median diameter of 1.3 micron. This was determined by preparation of an aqueous 0.5% ammonium fluorescein solution. This solution was aspirated at 8 psi to produce the aerosol droplets. The droplets were spray-dried in air and the resulting particulate was collected on 0.2-micron Nuclepore filters. Microscopic examination of the filters showed a mean particle size of 1.3 micron.

Prior to sample collection, it was necessary to determine the amount of dilution air needed to dilute the aspirator output to produce the desired concentration levels. This was necessary, because simultaneous monitoring of the generator output was not possible.

Samples were collected and analyzed to monitor the concentration in the sampling chamber prior to collection of the 2X level samples. When the correct amount of dilution air was added to give approximately the 2X level, six samples were taken.

The aspirator output of 24 liters per minute at 8 psi was diluted with air at 23.5, 47.0, and 94 liters/minute to obtain the 2X, 1X, and 0.5X levels, respectively. Samples were collected for 15 minutes at a flow rate of 1.5 liter/minute.

Collection Efficiency

Collection efficiency at a concentration of 0.90 mg/cu m was determined by measuring the amount of particulate collected on each of the two filters in series mounted in direct contact with each other. The collection efficiency of the filter was found to be 1.00 at a detection limit of 0.012 mg/cu m. Thus, no correction for collection efficiency is needed in this method.

Time Study

To determine the stability of soluble chromic compounds (most importantly soluble hexavalent chromium compounds) on an organic filter, a time study was done at the 1X OSHA level. Six filters were spiked with 45 micrograms of chromium from an aqueous solution of 3.18 mg/ml potassium dichromate. The filters were stored in screw cap vials for seven days and then analyzed. The average recovery was 1.043 with a CV_1 of 0.047. Therefore, soluble chromium compounds, especially the more reactive hexavalent chromium, are stable on MCEF filters for at least one week.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$$\overline{CV}_1 = 0.042 \qquad \overline{CV}_2 = 0.066 \qquad \overline{CV}_T = 0.085$$

Data Sheet: Chromium, Soluble Chromic and Chromous Salts as Cr, S323

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
23.6	22.0	0.932	44.0	42.0	0.955	90.0	93.0	1.033
23.6	22.0	0.932	44.0	43.0	0.977	90.0	95.0	1.056
23.4	22.5	0.962	44.0	46.0	1.046	90.0	89.0	0.989
23.4	23.5	1.004	44.0	43.0	0.977	90.0	94.0	1.044
22.4	23.5	1.049	44.0	43.0	0.977	90.0	90.0	1.000
22.4	24.0	1.071	44.0	42.0	0.955	90.0	90.2	1.002
n =		6			6			6
mean		0.992			0.981			1.021
std dev		0.060			0.034			0.027
CV_1		0.060			0.035			0.026

$\overline{CV}_1$ 0.043

$\overline{CV}_{A+AMR}$ 0.046

Based on these results, no analytical method recovery correction is necessary.

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Data Sheet: Chromium, Soluble Chromic and Chromous Salts as Cr
S323

Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m*
0.5S	27.0	86.8	0.311
	27.0	89.9	0.300
	27.0	87.8	0.308
	23.0	89.9	0.256
	23.0	90.0	0.256
	23.0	87.5	0.263
		n = 6	
		mean	0.282
		std dev	0.027
		CV_2	0.096
1S	45.0	86.8	0.518
	44.0	89.9	0.489
	45.0	87.8	0.513
	44.0	89.9	0.489
	42.0	90.0	0.467
	45.0	87.5	0.514
		n = 6	
		mean	0.498
		std dev	0.020
		CV_2	0.040
2S	81.4	86.8	0.938
	86.6	89.9	0.963
	81.4	87.8	0.927
	90.8	89.9	1.010
	79.2	90.0	0.880
	84.4	87.5	0.965
		n = 6	
		mean	0.947
		std dev	0.044
$\overline{CV}_2$ 0.066		CV_2	0.046

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Methyl Chloroform (1,1,1-Trichloroethane), No. S328

OSHA Standard: 1900 mg/cu m

Chemical used for validation: 1,1,1-Trichloroethane, inhibited; Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S328 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methyl chloroform represented in a 3-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using octane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 374 mg/min of methyl chloroform via a syringe injector to a dry air stream flowing at a rate of 0.0987 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 15 minutes (3.3 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 36.2 mg of methyl chloroform when a test atmosphere containing 3790 mg/cu m of methyl chloroform in air was sampled at 0.187 liters per minute for 51 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0182 \qquad \overline{CV}_2 = 0.0199 \qquad \overline{CV}_T = 0.0543$$

The average recovery of the generated samples over all levels was

$$99.5 \pm 7.3\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methyl Chloroform S328

Analysis

Level mg added	0.5S mg found	DE	mg added	1S mg found	DE	mg added	2S mg found	DE
2.915	2.960	1.015	5.83	5.65	0.969	11.40	11.41	1.001
2.915	2.804	0.962	5.83	5.49	0.942	11.40	11.20	0.983
2.915	2.857	0.980	5.83	5.68	0.974	11.40	11.23	0.985
2.915	2.960	1.015	5.83	5.76	0.988	11.40	11.42	1.002
2.915	2.924	1.003	5.83	5.84	1.002	11.40	11.35	0.996
2.915	2.911	0.999	5.83	5.78	0.991	11.40	11.47	1.006
n =		6			6			6
mean		0.996			0.978			0.996
std dev		0.0209			0.0212			0.0095
CV_1		0.0210			0.0216			0.00954

$\overline{CV}_1$ 0.0182

$\overline{CV}_{A+\overline{DE}}$ 0.0197

Data Sheet: Methyl Chloroform S328

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.968	3.01	3.37	893	904	
	*	--	--	--	904	
	3.030	3.08	3.37	914	904	
	3.157	3.21	3.37	953	904	
	2.960	3.01	3.37	893	904	
	2.960	3.01	3.37	893	904	
			n = 5			
			mean	909		100.6
			std dev	26.12		
			CV_2	0.0287		
1S	5.95	6.04	3.37	1792	1863	
	5.99	6.08	3.34	1820	1863	
	5.95	6.04	3.31	1825	1863	
	6.17	6.26	3.43	1825	1863	
	6.14	6.23	3.38	1843	1863	
	6.16	6.25	3.35	1866	1863	
			n = 6			
			mean	1829		98.2
			std dev	24.68		
			CV_2	0.0135		
2S	12.85	13.05	3.47	3761	3790	
	12.62	12.81	3.38	3790	3790	
	12.42	12.61	3.38	3731	3790	
	12.42	12.61	3.37	3742	3790	
	12.84	13.04	3.50	3726	3790	
	12.94	13.14	3.38	3888	3790	
			n = 6			
			mean	3773		99.6
			std dev	61.0		
			CV_2	0.0162		
			$\overline{CV}_2$	0.0199		

* Sample lost.

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Backup Data Report

Substance: Methylene Chloride, No. S329

OSHA Standard: 3475 mg/cu m (Ceiling); 1740 mg/cu m (T.W.A.)
6950 mg/cu m (Peak-maximum duration of 5 minutes in any two hours)

Chemical used for validation: Methylene Chloride, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S329 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methylene chloride represented in a 0.75-liter air sample. The charcoal used was Lot 105 (100 mg front and 50 mg backup) activated coconut charcoal supplied by SKC, INC., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using decane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 was modified in that the recommended sampling tube consists of two separate tubes containing the 100-mg front and 50-mg backup sections. This modification is recommended because methylene chloride is a solvent with a high vapor pressure and therefore the probability of migration exists. Note, however, that migration was not actually tested in these studies.

Generation

Test atmosphere samples at a concentration 2 times the OSHA ceiling level were generated by delivering 709.5 mg/min of methylene chloride via a syringe injector to a dry air stream flowing at a rate of 0.1000 cu m/min. The three sample lines were then maintained at dilution ratios of 0.240, 0.499, and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.050 liters per minute for 15 minutes (0.75 liters); the sampling tubes used consisted of two separate front and backup tubes. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 23.3 mg of methylene chloride when a test atmosphere containing 6727 mg/cu m of methylene

chloride in air was sampled at 0.187 liters per minute for 18.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

The above breakthrough experiments were done on a different day than the collected samples.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0261 \qquad \overline{CV}_2 = 0.0527 \qquad \overline{CV}_T = 0.073$$

The average recovery of the generated samples over all levels was

$$95.3 \pm 8.8\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methylene Chloride, S329

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.325	1.328	1.002	2.650	2.565	0.968	5.300	5.197	0.981
1.325	1.326	1.001	2.650	2.398	0.905	5.300	5.151	0.972
1.325	1.294	0.977	2.650	2.555	0.964	5.300	5.231	0.987
1.325	1.306	0.986	2.650	2.612	0.986	5.300	5.142	0.970
1.325	1.256	0.948	2.650	2.499	0.943	5.300	5.225	0.986
1.325	1.370	1.034	2.650	2.605	0.983	5.300	5.037	0.950
n =		6			6			6
mean		0.991			0.958			0.974
std dev		0.0288			0.0303			0.0138
CV_1		0.0290			0.0316			0.0142

$\overline{CV}_1$ 0.0261

$\overline{CV}_{A+\overline{DE}}$ 0.0282

Data Sheet: Methylene Chloride, S329

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.471	1.510	0.991	1524	1700	
	1.534	1.575	0.977	1612	1700	
	1.614	1.657	1.031	1607	1700	
	1.648	1.692	1.061	1595	1700	
	1.685	1.730	1.068	1620	1700	
	1.439	1.477	1.046	1412	1700	
			n = 6			
			mean	1560		91.8
			std dev	81.1		
			CV_2	0.0520		
1S	3.40	3.49	1.004	3480	3540	
	3.46	3.55	0.991	3580	3540	
	3.29	3.38	0.991	3410	3540	
	3.22	3.31	0.964	3430	3540	
	3.14	3.22	0.977	3300	3540	
	3.25	3.34	0.977	3420	3540	
			n = 6			
			mean	3440		97.2
			std dev	91.8		
			CV_2	0.0267		
2S	5.61	5.76	0.964	5980	7100	
	6.75	6.93	0.977	7090	7100	
	6.76	6.94	0.991	7000	7100	
	7.29	7.49	1.046	7160	7100	
	6.73	6.91	0.964	7170	7100	
	*1.17	-	0.977	-	7100	
			n = 5			
			mean	6880		96.9
			std dev	507.0		
			CV_2	0.0737		
			$\overline{CV}_2$	0.0527		

*These values excluded from statistical analysis

Backup Data Report

Substance:	Phenol, No. S330
OSHA Standard:	5 ppm (19 mg/cu m)--skin
Chemical Used for Validation:	Phenol, Lot 2858 J. T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of phenol in air is described in NIOSH Method S330. The method is a combination of bubbler collection and gas chromatographic analysis of the collected samples. Phenol is collected in 15 ml of 0.1 N sodium hydroxide and later acidified with sulfuric acid. Samples of phenol were generated by the procedure described below in midget bubblers containing 15 ml of the collection medium. Analysis of the generated samples was done by gas chromatography. The "found" concentrations of phenol in air were determined by dividing mg found by the sample volume (critical orifice flow rate for that sample X 110 minutes). The "true" concentrations of phenol in the generated samples were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. All three levels were monitored with a total hydrocarbon analyzer to determine that the rates of generation were constant.

Generation

Samples of phenol were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte dissolved in ethanol (1.3 g phenol per gram of ethanol) and delivered into a heated oven packed with glass beads. Nitrogen introduced into the oven at a rate of 7.74 liters/minute carried the analyte out of the first stage of the generator. A heat lamp was used to heat the analyte in this area. Dilution air at a rate of 20.1 liters/minute was used to dilute the vapor to the 2X OSHA standard level. Dilutions were again made to obtain the 1X and 0.5X OSHA standard levels. The dilution system is described in Reference No. 1.

The concentrations in the three sampling chambers were determined by using the delivery rate of the syringe drive and known flow rates of the dilution air.

Samples were collected for 110 minutes at a rate of approximately 1.0 liter per minute (individual critical orifices vary slightly in flow rate).

Collection Efficiency

A collection efficiency experiment was performed at 37.8 mg/cu m to test the ability of a single bubbler to trap phenol vapors. Two bubblers, each containing 15 ml of the collection medium, were connected in series. The gas stream passing through the front bubbler was bubbled through a second bubbler. Thus, any phenol vapor not collected in the front bubbler would be trapped in the second bubbler, allowing determination of the efficiency of the front bubbler. The front and backup bubbler solutions were analyzed. The collection efficiency was found to be 1.00 ± 0.01.

Discussion

Because ethanol was used in the generation of phenol, it was necessary to test if ethanol would interfere with phenol on the gas chromatogram. A solution containing 38 microliters phenol/25 ml ethanol was used, and it was discovered that ethanol does not interfere.

A time study at 1X the OSHA standard level was conducted by spiking six samples of 15 ml of 0.1 N sodium hydroxide in 25-ml volumetric flasks. The samples were allowed to stand for 5 days and were analyzed on the fifth day. No concentration changes during this time period were found.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$$\overline{CV}_1 = 0.044 \qquad \overline{CV}_2 = 0.043 \qquad \overline{CV}_T = 0.068$$

There was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Phenol S330

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	Recovery (%)	mg taken	mg found	Recovery (%)	mg taken	mg found	Recovery (%)
0.950	0.880	92.6	1.90	1.67	87.9	3.80	3.75	98.7
0.950	0.866	91.2	1.90	1.86	97.9	3.80	3.84	101.1
0.950	0.994	104.6	1.90	1.79	94.2	3.80	3.84	101.1
0.950	0.982	103.4	1.90	1.83	96.3	3.80	3.82	100.5
0.950	0.974	102.5	1.90	1.83	96.3	3.80	3.82	100.5
0.950	1.003	105.6	1.90	1.86	97.9	3.80	3.73	98.2
n =		6			6			6
mean		100.0			95.1			100.0
std dev		6.4			3.8			1.3
CV_1		0.064			0.040			0.013

$\overline{CV}_1$ 0.044

$\overline{CV}_{A+\overline{DE}}$ 0.048

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Data Sheet: Phenol S330

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5S	0.936	102.3	9.15	9.46	
	0.782	92.9	8.42	9.46	
	0.895	100.4	8.91	9.46	
	0.861	100.0	8.61	9.46	
	0.900	106.5	8.45	9.46	
	0.870	99.2	8.77	9.46	
		n = 6			
		mean	8.72		92.2
		std dev	0.28		
		CV_2	0.032		
1S	1.782	101.9	17.49	18.92	
	1.753	89.5	19.59	18.92	
	1.638	96.4	16.99	18.92	
	1.816	96.4	18.84	18.92	
	1.736	88.0	19.73	18.92	
	1.694	94.9	17.85	18.92	
		n = 6			
		mean	18.42		97.4
		std dev	1.14		
		CV_2	0.062		
2S	3.57	102.3	34.9	37.8	
	3.48	95.9	36.3	37.8	
	3.52	101.1	34.8	37.8	
	3.26	97.0	33.6	37.8	
	3.51	99.2	35.4	37.8	
	3.31	92.6	35.7	37.8	
		n = 6			
		mean	35.1		92.9
		std dev	0.9		
$\overline{CV}_2$ 0.043		CV_2	0.026		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Phosphoric Acid, No. S333

OSHA Standard: 1.0 mg/cu m

Chemical used for validation: Phosphoric Acid, 85%, Fisher Scientific Co.

Procedure

The general procedure used is described in NIOSH Method No. S333 which is a combination and modification of P&CAM 173 for filter collection of particulates and P&CAM 216for the analysis of phosphoric acid. The reliability of the analytical method was tested at sample concentrations equal to that present in a 90-liter sample at 0.5, 1, and 2 times the OSHA standard. The appropriate aliquot of a solution of the analyte in water was added to 37 mm Type AA Millipore filters. The analyte was leached from the filter with hot water and analyzed spectrophotometrically with a Beckman Model DU Spectrophotometer. The six samples of each of the 0.5, 1, and 2 times the OSHA standard concentration were collected simultaneously. Details of the leaching and analysis procedures may be found in Section 8.4 of NIOSH Method No. S333.

Modification

P&CAM 216 for the analysis of phosphoric acid was modified to improve the recovery of phosphoric acid. The cold water leaching step specified in P&CAM 216 , Section 8.3.1, was found to be satisfactory for recovery of the mono-potassium salt of phosphoric acid, but gave low recovery (85%) of phosphoric acid (Table 1). Hot water was substituted for the leaching step, Section 8.4.2 of the present method.

Generation

Test atmospheres at a concentration 2X the OSHA standard level were generated by atomization of a solution of 85% phosphoric acid in water containing 11.790 g/liter as phosphoric acid into a dry solvent-free air stream flow. The atomizer flowrate was 9 liters per minute; aerosol from the atomizer was diluted with 84 liters per minute of dry solvent-free air. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline; twofold and fourfold dilutions were then made to obtain 1 and 0.5 times the OSHA standard level. All six samples at the 3 test levels were collected simultaneously at 1.5 liters per minute for 60 minutes (90 liters). Since collection efficiency was found to be 1.00 $\pm$ 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate phosphoric acid was determined by collecting six filter samples at an air sample concentration of 1.93 mg/cu m. Two filters were mounted back to back in contact with each other and supported by the backup pad.

The data in the Sampling and Analysis Data Sheet shows that the filter collection efficiency for phosphoric acid is 99.4% (Table 2).

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for phosphoric acid using the equation shown in Reference 2.

The sampling and analysis data gave a chi squared value of 10.0 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for phosphoric acid, however, show excellent precision and pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0348 \qquad \overline{CV}_2 = 0.0174 \qquad \overline{CV}_T = 0.055$$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

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TABLE 1

Data Sheet: Phosphoric Acid, S333
(Cold Water Leach)

Analysis

Level	0.5S		1S		2S	
µg added		µg found	µg added	µg found	µg added	µg found
45.0		38.4	90.0	80.0	180	172.8
45.0		35.5	90.0	75.3	180	166.8
45.0		28.4	90.0	72.6	180	170.7
45.0		28.4	90.0	74.5	180	167.5
45.0		28.7	90.0	74.3	180	164.3
45.0		36.1	90.0	73.6	180	162.4
n =		6		6		6
mean		32.6		75.1		167.4
std dev		4.58		2.59		3.87
CV_1		0.140		0.034		0.023
% Recovery		72.4		83.4		93.0

$$\overline{CV}_1 = 0.084$$

Average Recovery = 82.9%

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TABLE 2

Phosphoric Acid Collection Efficiency

------- µg Found on Filter -----			
Front	Backup	Total	% Found in Front
180.8	1.6	182.4	99.1
*	0.6		
176.7	1.6	178.3	99.1
179.7	1.0	180.7	99.4
178.8	0.1	178.9	99.9
180.8	0.6	181.4	99.7

Average Collection Efficiency 99.4%

* Sample lost

Data Sheet: Phosphoric Acid, S333
(Hot Water Leach)

Analysis

Level	0.5S		1S			2S		
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
45.0	42.4	0.942	90.0	89.9	0.999	180.0	178.0	0.989
45.0	49.9	1.109	90.0	93.0	1.033	180.0	177.2	0.984
45.0	44.6	0.991	90.0	89.3	0.992	180.0	178.0	0.989
45.0	44.4	0.987	90.0	89.8	0.998	180.0	178.0	0.989
45.0	44.6	0.991	90.0	87.8	0.976	180.0	172.9	0.961
45.0	45.2	1.004	90.0	87.8	0.976	180.0	176.4	0.980
n =		6			6			6
mean		1.004			0.996			0.982
std dev		0.0557			0.0210			0.0109
CV_1		0.0554			0.0210			0.0111

$$\overline{CV}_1 = 0.0348$$

$$\overline{CV}_{A+\overline{CE}} = 0.0376$$

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Data Sheet: Phosphoric Acid, S333
Sampling and Analysis

Test Level	Found		
	µg	Liters	mg/cu m
0.5S	45.2	92.1	0.491
	42.6	91.8	0.464
	42.4	91.5	0.463
	42.4	92.2	0.460
	43.5	91.7	0.474
	42.2	92.5	0.456
		n = 6	
		mean	0.468
		std dev	0.0128
		CV_2	0.0273
1S	88.9	92.3	0.963
	87.8	92.4	0.950
	87.4	91.9	0.951
	87.8	92.6	0.948
	88.1	93.0	0.947
	87.6	92.5	0.947
		n = 6	
		mean	0.951
		std dev	0.0061
		CV_2	0.0064
2S	180.8	92.3	1.959
	*	*	*
	176.7	92.2	1.916
	179.7	92.1	1.951
	178.8	92.0	1.943
	180.8	93.8	1.928
		n = 5	
		mean	1.939
		std dev	0.0174
		CV_2	0.0090
		$\overline{CV}_2$	0.0174

*Sample Lost

Backup Data Report

Substance: Tetrachloroethylene, No. S335

OSHA Standard: 680 mg/cu m (T.W.A.)
1355 mg/cu m (Ceiling)
2035 mg/cu m (Peak - maximum duration of 5 minutes in any 2 hours)

Chemical used for validation: Tetrachloroethylene (inhibited with 0.5% ethanol) Lot No. D4A, Eastman Chemical Co.

Procedure

The general procedure used is described in NIOSH Method No. S335 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of tetrachloroethylene represented in a 3-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere camples at a concentration 2 times the OSHA standard level were generated by delivering 276 mg/min of tetrachloroethylene via a syringe injector to a dry air stream flowing at a rate of 0.1004 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 15 minutes (3.3 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 58.1 mg of tetrachloroethylene when a test atmosphere containing 2749 mg/cu m of tetrachloroethylene in air was sampled at 0.187 liters per minute for 113 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0115 \qquad \overline{CV}_2 = 0.0126 \qquad \overline{CV}_T = 0.0518$$

The average recovery of the generated samples over all levels was

$$92.8 \pm 7.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Tetrachloroethylene, S335

Analysis

Level	0.5S			1S			2S		
	mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
	2.109	1.952	0.926	4.22	4.21	0.998	8.44	7.93	0.940
	2.109	1.978	0.938	4.22	4.17	0.988	8.44	8.06	0.955
	2.109	2.003	0.950	4.22	4.13	0.979	8.44	8.08	0.957
	2.109	1.989	0.943	4.22	4.04	0.957	8.44	8.08	0.957
	2.109	2.169*	1.028*	4.22	4.07	0.964	8.44	8.05	0.954
	2.109	1.973	0.936	4.22	4.10	0.972	8.44	8.11	0.961
n =		5			6			6	
mean		0.939			0.976			0.954	
std dev		0.0089			0.0152			0.0073	
CV_1		0.0095			0.0156			0.0076	

$\overline{CV}_1$ 0.0115

$\overline{CV}_{A+\overline{DE}}$ 0.0125

* These values excluded from statistical analysis.

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Data Sheet: Tetrachloroethylene S335

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.991	2.118	3.36	630	655	
	2.008	2.136	3.36	636	655	
	1.991	2.118	3.36	630	655	
	2.003	2.131	3.36	634	655	
	1.951	2.076	3.36	618	655	
	1.931	2.054	3.36	611	655	
			n = 6			
			mean	627		95.7
			std dev	9.83		
			CV_2	0.0157		
1S	4.02	4.19	3.36	1246	1351	
	3.97	4.14	3.33	1242	1351	
	3.85	4.01	3.30	1215	1351	
	4.08	4.25	3.42	1243	1351	
	3.95	4.11	3.38	1217	1351	
	3.96	4.13	3.35	1231	1351	
			n = 6			
			mean	1232		91.2
			std dev	13.65		
			CV_2	0.0111		
2S	8.27	8.57	3.47	2470	2749	
	8.30	8.60	3.38	2545	2749	
	8.24	8.54	3.38	2526	2749	
	8.19	8.49	3.36	2526	2749	
	8.55	8.86	3.50	2531	2749	
	8.21	8.51	3.38	2517	2749	
			n = 6			
			mean	2519		91.6
			std dev	25.78		
			CV_2	0.0102		
			$\overline{CV_2}$	0.0126		

Backup Data Report

Substance: Trichloroethylene, No. S336

OSHA Standard: 535 mg/cu m (T.W.A.)
1075 mg/cu m (Ceiling)
1610 mg/cu m (Peak - maximum duration of 5 min. in any 2 hours)

Chemical used for validation: Trichloroethylene, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S336 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of trichloroethylene represented in a 3-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using octane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 219.3 mg/min of trichloroethylene via a syringe injector to a dry air stream flowing at a rate of 0.1008 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 15 minutes (3.3 liters). The data reported is for the second set of 18 samples collected. The first set of data was rejected because the recoveries at the 3 concentrations were low, with an average of 89.6% and a CV_2 = 0.0326 for 15 samples (5 acceptable samples only at each concentration). This low recovery is associated with problems in calibrating the generator concentration. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 41.95 mg of trichloroethylene when a test atmosphere containing 2266 mg/cu m of

trichloroethylene in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

The breakthrough data are based on a prior experiment.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for trichloroethylene as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 10.21 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for trichloroethylene show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0384 \qquad \overline{CV}_2 = 0.0636 \qquad \overline{CV}_T = 0.0824$$

The average recovery of the generated samples over all levels was

$$92.9 \pm 10.2\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Trichloroethylene, S336

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.601	1.422	0.888	3.20	3.03	0.947	6.40	6.18	0.966
1.601	1.624	1.014	3.20	3.17	0.991	6.40	6.11	0.955
1.601	1.536	0.959	3.20	3.17	0.991	6.40	6.05	0.945
1.601	1.440	0.899	3.20	3.04	0.950	6.40	6.12	0.956
1.601	1.661	1.037	3.20	3.08	0.963	6.40	6.14	0.959
1.601	1.585	0.990	3.20	3.12	0.975	6.40	6.13	0.958
n =		6			6			6
mean		0.965			0.970			0.957
std dev		0.0609			0.0194			0.00683
CV_1		0.0631			0.0200			0.00714

$\overline{CV}_1$ 0.0384

$\overline{CV}_{A+\overline{DE}}$ 0.0415

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Data Sheet: Trichloroethylene S336

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.592	1.658	3.38	491	519	
	1.588	1.654	3.38	489	519	
	1.570	1.635	3.38	484	519	
	1.503	1.566	3.38	463	519	
	1.612	1.679	3.38	497	519	
	1.417	1.476	3.38	437	519	
			n = 6			
			mean	476.8		91.9
			std dev	22.7		
			CV_2	0.0477		
1S	3.25	3.39	3.38	1003	1070	
	3.23	3.36	3.35	1003	1070	
	3.23	3.36	3.32	1012	1070	
	3.35	3.49	3.44	1015	1070	
	3.19	3.32	3.39	979	1070	
	2.75*	2.86*	3.36	851*	1070	
			n = 5			
			mean	1002		93.6
			std dev	14.14		
			CV_2	0.0141		
2S	7.03	7.32	3.48	2103	2176	
	6.32	6.58	3.39	1941	2176	
	5.69	5.93	3.39	1749	2176	
	2.27*	2.36*	3.38	698*	2176	
	6.84	7.13	3.51	2031	2176	
	7.33	7.64	3.32	2301	2176	
			n = 5			
			mean	2025		93.1
			std dev	203.4		
			CV_2	0.1005		
			$\overline{CV}_2$	0.0636		

* These values excluded from statistical analysis.

Backup Data Report

Substance:	Beryllium and Beryllium Compounds (as Be) No. S339
OSHA Standard:	5 µg/cu m - Ceiling 25 µg/cu m - Peak 2 µg/cu m - T.W.A.
Chemical Used for Validation:	High Purity Beryllium Metal (Johnson Matthey)

Procedure

The general procedure is described in NIOSH Method No. S339 which has been adapted from P&CAM 173. The validity of the analytical method was tested at sample concentrations representing 40-liter samples at 0.5, 1.0, and 2.0 times the OSHA ceiling standard. The appropriate aliquot of a solution of the analyte in dilute hydrochloric acid was added to 37-mm, 0.45-micron Type AA Millipore filters. The filters containing the samples were digested with concentrated nitric, concentrated sulfuric, and perchloric acids, and the analyte was dissolved in dilute hydrochloric acid. Analyses were done with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer equipped with a heated graphite atomizer, HGA Model 2000 and Deuterium Background Corrector. The absorbance, measured at 234.9 nm, was used as a measure of the beryllium concentration in the sample. A similar procedure was used for the analysis of 18 generated samples, 6 each at approximately 0.5, 1, and 2 times the OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S339.

Modification

P&CAM 173 was modified by use of perchloric and sulfuric acid to aid in decomposition of the filter material and by the use of a heated graphite atomizer furnace accessory to the atomic absorption spectrophotometer.

Generation

Test atmospheres were generated in the generator apparatus described in the attachment to the Nickel Report (Reference No. 1). Concentrations of approximately 2X, 1X, and 0.5X the OSHA standard level were generated by atomizing solutions of beryllium in dilute hydrochloric acid at concentrations such that the desired aerosol concentrations were achieved on separate runs. Each aerosol level was collected on 37-mm filters with flows of about 1.4 liters per minute for 30 minutes. Since collection efficiency was found to be 1.00, the concentration in the generator and the "found" concentrations were considered equal.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for particulate beryllium was determined by collecting eight filter samples at an air sample concentration of 11.84 µg/cu m (2X OSHA standard level). The physical arrangement of the filters was such that the two filters were mounted in contact with each other and supported by the support pad. The collection efficiency was considered to be 1.00 when the test atmosphere was sampled for 30 minutes. The data on the backup filter was obtained on a final assay solution volume of 5 ml rather than 10 ml as recommended in the NIOSH Method S339.

No correction for collection efficiency is necessary.

COLLECTION EFFICIENCY

2X Level

Front filter Found, µg	Backup Filter Found, µg	Collection Efficiency
0.510	N.D.	1.00
0.505	N.D.	1.00
0.510	N.D.	1.00
0.520	N.D.	1.00
0.492	N.D.	1.00
0.480	N.D.	1.00
0.488	N.D.	1.00
0.497	N.D.	1.00

N.D. = Not Detected (< 0.002 µg)

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.032$ $\overline{CV}_2 = 0.037$ $\overline{CV}_T = 0.064$

Data Sheet: Beryllium and Beryllium Compounds (as Be) S339

Analysis

Level	0.5S		1S			2S		
µg added	µg found	A.M.R.	µg added	µg found	A.M.R.	µg added	µg found	A.M.R.
0.1125	0.1150	1.022	0.225	0.233	1.036	0.450	0.480	1.067
0.1125	0.1250	1.111	0.225	0.245	1.089	0.450	0.462	1.027
0.1125	0.1260	1.120	0.225	0.230	1.022	0.450	0.480	1.067
0.1125	0.1220	1.084	0.225	0.233	1.036	0.450	0.497	1.104
0.1125	0.1300	1.156	0.225	0.233	1.036	0.450	0.477	1.060
0.1125	0.1230	1.093	0.225	0.242	1.076	0.450	0.463	1.029
n =		6			6			6
mean		1.098			1.049			1.059
std dev		0.045			0.027			0.029
CV_1		0.041			0.026			0.027

$\overline{CV}_1$ 0.032

$\overline{CV}_{A+\overline{AMR}}$ 0.035

An average Analytical Method Recovery (A.M.R.) of 1.069 was used to calculate the corr. µg in the Sampling and Analysis Table.

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Data Sheet: Beryllium and Beryllium Compounds (as Be) S339

Sampling and Analysis

Test Level		Found			
		µg	Corr µg	Liters	µg/cu m*
		0.1170	0.1094	40.2	2.721
		0.1100	0.1029	40.2	2.560
		0.1120	0.1048	38.1	2.751
		0.1170	0.1094	40.5	2.701
		0.1150	0.1076	38.7	2.780
		0.1120	0.1048	40.8	2.569
				n = 6	
				mean	2.680
				std dev	0.094
				CV_2	0.035
1S		0.2450	0.2292	40.2	5.70
		0.2330	0.2180	40.2	5.42
		0.2370	0.2217	38.1	5.82
		0.2450	0.2292	40.5	5.66
		0.2370	0.2217	38.7	5.73
		0.2330	0.2180	40.8	5.34
				n = 6	
				mean	5.61
				std dev	0.19
				CV_2	0.034
2S		0.510	0.477	40.2	11.87
		0.505	0.472	40.2	11.74
		0.510	0.477	38.1	12.52
		0.520	0.486	40.5	12.00
		0.492	0.460	38.7	11.89
		0.480	0.449	40.8	11.00
				n = 6	
				mean	11.84
				std dev	0.49
$\overline{CV}_2$	0.037			CV_2	0.041

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, Nickel, No. S206, prepared under NIOSH Contract No. CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract No. CDC-99-74-45.

Backup Data Report

Substance:	Lead and Inorganic Lead Compounds, No. S341
OSHA Standard:	0.2 mg/cu m
Chemical Used for Validation:	Lead Nitrate Mallinckrodt

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of lead and inorganic lead compounds in air is described in NIOSH Method No. S341, which has been adapted from P&CAM 173. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 180-liter sample at 0.5X, 1X, and 2X the OSHA standard. Appropriate aliquots (2, 4, and 8 microliters) of an aqueous 14.4 mg/ml lead nitrate solution were added to 37-mm/0.8 micron type AA MCEF filters. The filters were digested in concentrated nitric acid to remove the organic matrix. The ashed-analyte was then dissolved in 1 ml concentrated nitric acid and diluted to 10 ml with deionized water prior to AA analysis. Analyses were done on a Varian Techtron AA6 atomic absorption spectrophotometer. The absorbance, measured at 217 nm, was used as a measure of the lead concentration in the sample, when compared with samples of known concentrations. This procedure was used for the analysis of 18 generated samples, 6 at each of the three OSHA standard levels. Details of the analytical procedures may be found in Section 8.4 of NIOSH Method No. S341. Details of the generation of the analyte at the three concentration levels of 0.5, 1, and 2X the OSHA standard are described below.

Modifications

There were no major modifications made to P&CAM 173.

Generation

Samples of inorganic lead particulates were generated by the procedure described in Reference No. 1. A 0.5% aqueous solution of lead nitrate was used in the aspiration system. A pressure drop of 6 psi across the aspirator tip was used in the generation of the aerosol. This pressure gave particles with a median diameter of 1.3 microns. This was determined by preparation of an aqueous 0.5% ammonium fluorescein solution. The fluorescein was aspirated at 6.0 psi to produce the aerosol droplets. The droplets were spray-dried in air and the resulting particulate was collected on 0.2 micron Nuclepore filters. Microscopic examination of the filters showed a mean particle size of approximately 1.3 microns.

Prior to sample collection, it was necessary to determine the amount of dilution air needed to dilute the aspirator output to produce the desired concentration levels. This was necessary because direct simultaneous monitoring of the generator output for lead was not possible.

Samples were collected and analyzed to monitor the concentration in the sampling chamber prior to collection of the 2X level samples. When the correct amount of dilution air was added to give approximately the 2X level, six samples were taken.

The aspirator output of 21 liters per minute at 6 psi was diluted with air at 32, 63, and 100 liters/minute to obtain the 2X, 1X, and 0.5X OSHA levels, respectively.

Samples were collected at a flow rate of 1.5 liters per minute for 120 minutes.

Collection Efficiency

Collection efficiency at a concentration of 0.399 mg/cu m was determined by measuring the amount of particulates collected on each of two filters mounted in series in direct contact to each other. The collection efficiency of the filter was found to be 1.00 at a detection limit of 0.013 mg/cu m. Thus, no correction for collection efficiency is needed in the calculation of results.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.030$ $\overline{CV}_2 = 0.050$ $\overline{CV}_T = 0.072$

Data Sheet: Lead and Inorganic Lead Compounds S341

Analysis

Level	0.5S			1S			2S	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
18.0	18.0	1.000	36.0	35.0	0.972	72.0	70.0	0.972
18.0	17.0	0.944	36.0	35.0	0.972	72.0	73.0	1.014
18.0	17.0	0.944	36.0	35.0	0.972	72.0	70.0	0.972
18.0	19.0	1.056	36.0	36.0	1.000	72.0	68.0	0.944
18.0	18.0	1.000	36.0	36.0	1.000	72.0	72.0	1.000
18.0	18.0	1.000	36.0	35.0	0.972	72.0	72.0	1.000
n =		6			6			6
mean		0.991			0.981			0.984
std dev		0.042			0.014			0.026
CV_1		0.042			0.014			0.026

$\overline{CV}_1$ 0.030

$\overline{CV}_{A+\overline{AMR}}$ 0.032

Based on these results, no analytical method recovery correction is necessary.

Data Sheet: Lead and Inorganic Lead Compounds S341

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m*
0.5S	0.0227	173.7	0.1307
	0.0226	179.8	0.1257
	0.0227	175.0	0.1297
	0.0230	179.8	0.1279
	0.0233	180.0	0.1294
	0.0219	175.1	0.1251
		n = 6	
		mean	0.1281
		std dev	0.0023
		CV_2	0.018
1S	0.0370	173.7	0.2130
	0.0375	179.8	0.2086
	0.0315	175.0	0.1800
	0.0357	179.8	0.1986
	0.0360	180.0	0.2000
	0.0315	175.1	0.1799
		n = 6	
		mean	0.1967
		std dev	0.0140
		CV_2	0.071
2S	0.0710	173.7	0.409
	0.0685	179.8	0.381
	0.0677	175.0	0.387
	0.0750	179.8	0.417
	0.0685	180.0	0.381
	0.0730	175.1	0.417
		n = 6	
		mean	0.399
		std dev	0.018
$\overline{CV}_2$ 0.050		CV_2	0.045

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

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References

1. Backup Data Report, Terphenyls, No. S27, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Toluene, No. S343
OSHA Standard:	Ceiling - 300 ppm Peak - 500 ppm 8-hr. T.W.A. - 200 ppm
Chemical Used for Validation:	Toluene, A.R. Mallinckrodt

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of toluene in air is described in NIOSH Method S343, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA ceiling standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of toluene to represent 2-liter air samples. Samples of toluene in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The temperature and pressure were 22°C and 766 mm Hg. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of toluene in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample x 10 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA ceiling standard levels were determined using bag standards and a total hydrocarbon analyzer. The total hydrocarbon analyzer was also used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

One major modification was made to P&CAM 127. A hexane solution of toluene containing 563.6 μg/μl was used to apply the analyte onto the charcoal.

Generation

Samples of toluene were generated by the procedure described in Reference No. 1 using the 2-piece vapor generator. The generator conditions used are given below:

Nitrogen flow rate:	1.28 liter per minute at 22°C
Dilution air flow rate:	37.8 liters per minute at 22°C

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using bag standards and comparing the bag standard response with the chamber responses on the total hydrocarbon analyzer. Samples were collected for 10 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test. Breakthrough, 5% of the generated concentration of 2294 mg/cu m in the effluent, was observed after 62.6 minutes of sampling at a rate of 0.19 liter per minute at which time the test was discontinued.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.011$ $\overline{CV}_2 = 0.015$ $\overline{CV}_T = 0.052$

The average recovery at the OSHA ceiling standard level was 103.8%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Toluene S343

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.127	1.088	0.965	2.254	2.267	1.006	4.51	4.45	0.987
1.127	1.104	0.980	2.254	2.241	0.994	4.51	4.54	1.007
1.127	1.102	0.978	2.254	2.253	1.000	4.51	4.46	0.989
1.127	1.110	0.985	2.254	2.226	0.988	4.51	4.48	0.993
1.127	1.135	1.007	2.254	2.209	0.980	4.51	4.48	0.993
1.127	1.121	0.995	2.254	2.256	1.001	4.51	4.49	0.996
n =		6			6			6
mean		0.985			0.995			0.994
std dev		0.015			0.010			0.007
CV_1		0.015			0.010			0.007

$\overline{CV}_1$ 0.011

$\overline{CV}_{A+\overline{DE}}$ 0.012

The equation D.E. = $0.995 - e^{-4.11 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

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Data Sheet: Toluene S343

Sampling and Analysis

Test Level	Found					Taken	
	mg	Corr mg	Liters	mg/cu m	ppm	ppm	Recovery (%)
0.5S	1.059	1.078	1.96	550	143.4	145.5	
	1.092	1.110	2.01	552	143.9	145.5	
	1.111	1.128	2.06	548	142.9	145.5	
	1.003	1.024	1.92	533	139.0	145.5	
	0.943	0.968	1.71	566	147.6	145.5	
	1.048	1.067	1.93	553	144.2	145.5	
			n = 6				
			mean		143.5		98.6
			std dev		2.8		
			CV_2		0.020		
1S	1.976	1.986	1.70	1168	304	291	
	2.141	2.152	1.88	1145	298	291	
	1.544	1.555	1.57	990	258*	291	
	1.928	1.937	1.70	1139	297	291	
	2.016	2.026	1.73	1171	305	291	
	2.086	2.097	1.79	1172	306	291	
			n = 5				
			mean		302		103.8
			std dev		4		
			CV_2		0.013		
2S	4.54	4.56	2.00	2280	594	582	
	4.47	4.49	1.95	2303	600	582	
	4.19	4.21	1.85	2276	593	582	
	4.21	4.23	1.85	2287	596	582	
	4.07	4.09	1.75	2337	609	582	
	4.23	4.25	1.85	2297	599	582	
			n = 6				
			mean		598		102.8
			std dev		6		
$\overline{CV}_2$	0.015		CV_2		0.010		

* This value was deleted, because it did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Boron Oxide, No. S349

OSHA Standard: 15 mg/cu m

Chemical Used for Validation: None: basic gravimetric method validated for carbon black:

The method recommended is a gravimetric analysis. The gravimetric procedure is basically a simple and straightforward method. Consequently, the basic validation for all gravimetric methods was carried out using carbon black as an example. The carbon black studies were carried out over the concentration range appropriate for boron oxide. The complete details on the procedure, generation, collection efficiency, precision and accuracy of the method may be found in the S262 Carbon Black Backup Data Report (Reference 2, attached). The analytical method is described in NIOSH Method No. S349.

NIOSH guidelines for collection and analysis of particulate matter by gravimetric methods have been to limit filter loadings to 2 mg/filter, in order to avoid handling losses. In order to prevent exceeding this value at twice the nuisance dust standard level, sampling should be restricted to 60 liters at 1 liter per minute.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Carbon Black, Backup Data Report No. S262

ATTACHMENT TO BORON OXIDE

Backup Data Report

Substance: Carbon Black, No. S262

OSHA Standard: 3.5 mg/cu m

Chemical Used for Validation: Vulcan XC 72, Cabot Corporation

Introduction

The method for carbon black, as well as some other compounds otherwise classified as nuisance dust, is gravimetric. Thus, the experimental studies with carbon black were done to include compounds with an OSHA standard equal to 15 mg/cu m in order to satisfy the experimental and statistical criteria, not only for carbon black but also for other analytes in the nuisance dust category.

The experimental work for gravimetric methods, and carbon black in particular, was done with a 25 mm, 2.0 micrometer PVC filter and filter holder with integral stainless steel support screen. This filter size was used because a 37 mm, 2.0 micrometer PVC filter was not available at the time. Since the time of the studies reported here, however, a 37 mm, 2.0 micrometer PVC filter has become available Therefore, use of a conventional 37 mm filter cassette assembly is recommended for these methods. The filters should be supported by a stainless steel support screen. The collection efficiency of this filter type and arrangement is expected to be the same and the use of a larger diameter filter will prevent overloading of the filter.

Procedure

The general procedure used is described in NIOSH Method No. S262 which is an adaptation of the filter collection of particulates except that for these particular validation studies, the analyte was collected on tared 25 mm, Type BS Millipore (2.0 micrometer pore size PVC) filters. The filters were dried to constant weight over Drierite for at least 12 hours, and weighed to determine the mass of sample collected. The recommended method is simply a gravimetric method and therefore the preparation of 18 analytical, or spiked, samples was omitted. However, the procedure was verified by the gravimetric analysis of 18 generated samples, 6 at each of the 0.5, 1 and 2X OSHA standard levels for a 200-liter sample. Gravimetric analyses were carried out with a Mettler M5 Microbalance. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method S262.

Modification

The filter recommended is 2.0 µm pore size polyvinyl chloride, 27 mm, instead of the 37 mm cellulose ester membrane filter because the latter tends to absorb moisture and is not suitable for gravimetric analysis.

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Generation

The basic system used to generate test atmospheres of carbon black is described in detail in Appendix A.

For the generation of each of the test levels studied, approximately one gram of carbon black powder was loaded and compressed lightly by hand into the dust holder. The concentration of the carbon black in the chamber was then controlled by proper adjustment of the dust holder advance rate. The system allows for the simultaneous collection of 12 samples; however, only 6 samples at each test level were collected and analyzed. Particulate atmospheres prepared in this manner using the Wright Dust Feeder normally produce particles in the respirable size fraction range. The average particle size of the Vulcan XC 72 carbon black was 0.03 microns. The sampling rate was 1.7 liters per minute. Since collection efficiency was found to be 1.00 ± 0.01, the concentrations in the generator and the "found" concentration were considered to be equal. (Refer to Tables 1 and 2.) The range of atmospheric temperature and pressure during these studies were respectively 18-25°C and 749-761 mm Hg.

Discussion

The validation studies for carbon black were conducted in order to assess the gravimetric method not only for the analysis of carbon black but also for the analysis of other nuisance dusts as well, including boron oxide, and amorphous silica. Thus, the gravimetric analysis of carbon black was studied at 6 test concentration levels to simulate the equivalent of 0.5, 1 and 2X OSHA standard for carbon black (OSHA standard = 3.5 mg/cu m) using a 200-liter sample and a parallel equivalent for the nuisance dusts (OSHA standard = 15 mg/cu m) using a 100-liter sample. The sample volume tested in conjunction with these two OSHA standards was adjusted such that the sample size collected would represent a weighable amount of particulate but would minimize the danger of overloading the filter which can cause problems with the pump and also with sample flaking off the filter during handling and gravimetric analysis. The data for these samples are summarized in Tables 3 and 4.

The NIOSH recommended guidelines for the collection and gravimetric analysis of particulate have been to limit filter loadings to 2 mg/filter, in order to prevent handling losses. In order to prevent exceeding this value at the nuisance dust concentration levels, (Table 4), sampling should be restricted to 60 liters at 1 liter per minute. Sampling at these conditions would yield gravimetric data comparable to the weights in Table 3. Observe that the precision, $\overline{CV}_2$, for sample weights in the range of 0.4 - 1.6 mg (Table 3) is in excellent agreement with the precision of samples in the range of 0.8 - 2.9 mg (Table 4). The values were 0.0254 and 0.0258 respectively.

TABLE 1

Collection Efficiency: Carbon Black, S262

Generator Concentration: 6.3 mg/cu m
Sample Volume: 210 liters at 1.7 liters per minute

-------- µg Found ----------			
Front	Backup	Total	% Collected in Front
1332	13	1345	99.0
1307	22	1329	98.3
1322	14	1336	99.0
1349	44	1393	96.8
1321	15	1336	98.9
1228	- 2	1226	100.2

Average Collection Efficiency . . . 98.7%

TABLE 2

Collection Efficiency: Carbon Black, S262
For Nuisance Dust Levels, OSHA Standard = 15 mg/cu m

Generator Concentration: 28 mg/cu m
Sample Volume: 105 liters at 1.7 liters per minute

µg Found			
Front	Backup	Total	% Collected in Front
2858	0	2858	100.0
2909	2	2911	99.9
2970	- 1	2969	100.0
2885	4	2889	99.9
2892	- 1	2891	100.0
2990	- 6	2984	100.2

Average Collection Efficiency . . 100.0%

TABLE 3

Data Sheet: Carbon Black, S262
(25-mm PVC Filter)

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	401	213.5	1.878
	384	209.4	1.834
	414	208.2	1.988
	391	210.0	1.862
	382	213.2	1.792
	367	205.8	1.783
		n = 6	
		mean	1.856
		std dev	0.0746
		CV_2	0.0402
1S	710	212.5	3.34
	701	213.5	3.28
	685	208.2	3.29
	725	214.4	3.38
	703	210.0	3.35
	708	213.2	3.32
		n = 6	
		mean	3.33
		std dev	0.0378
		CV_2	0.0113
2S	1620	210.7	7.69
	1595	211.9	7.53
	1644	212.6	7.73
	1601	204.7	7.82
	1630	208.8	7.81
	1627	210.9	7.71
		n = 6	
		mean	7.71
		std dev	0.1050
		CV_2	0.0136
		$\overline{CV}_2$	0.0254

TABLE 4

Data Sheet: Carbon Black, S262
For Nuisance Dust Levels, OSHA Standard = 15 mg/cu m

Sampling and Analysis

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	785	105.6	7.43
	847	106.1	7.98
	829	104.1	7.96
	822	103.5	7.94
	854	106.6	8.01
	812	106.0	7.66
		n = 6	
		mean	7.83
		std dev	0.2336
		CV_2	0.0298
1S	2299	114.9	20.01
	2232	110.5	20.20
	2153	112.7	19.10
	2267	112.3	20.19
	2191	113.1	19.37
	2279	113.9	20.01
		n = 6	
		mean	19.81
		std dev	0.463
		CV_2	0.0234
2S	2858	105.8	27.01
	2909	106.4	27.34
	2970	102.7	28.92
	2885	104.8	27.53
	2892	104.4	27.70
	2990	107.3	27.87
		n = 6	
		mean	27.73
		std dev	0.655
		CV_2	0.0236
		$\overline{CV}_2$	0.0258

Collection Efficiency

Two sets of 6 generated samples collected on 25-mm Type BS Millipore filters were used for these studies. One set of samples represents a test atmosphere concentration of 6.3 mg/cu m sampled at 1.7 liters per minute for 120 minutes (210 liters) and the other is for a concentration of 28 mg/cu m sampled at 1.7 liters per minute for 60 minutes (105 liters). The front and backup filters were arranged in the 25-mm filter cassette holder such that the two filters were mounted back to back and in contact with each other; the filters were supported by a 25-mm, stainless steel screen. The average collection efficiencies were 99% and 100% respectively for the test atmospheres containing 6.3 mg/cu m and 28 mg/cu m. (Refer to Tables 1 and 2.)

Precision and Accuracy

The statistical procedures are described in Reference 1; calculations were based on the data summarized in Tables 3 and 4.

For carbon black, OSHA standard = 3.5 mg/cu m.

$$\overline{CV}_2 = 0.0254 \qquad \overline{CV}_T = 0.0561$$

For nuisance dust, OSHA standard = 15 mg/cu m.

$$\overline{CV}_2 = 0.0258 \qquad \overline{CV}_T = 0.0563$$

Since the collection efficiency was found to be at least 99%, the values found also represent the generator concentration. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Appendix A

Description of Dust Atmosphere Generation Apparatus

The basic elements of the system used to generate the dust test atmospheres are shown in Figures 1 and 2. The system consists of a Wright Dust Feeder, an aerosol charge neutralizer, and an 80-liter stainless dust chamber.

Dust samples to be dispersed in the apparatus are compressed into a container which is attached to the Wright Dust Feeder. In operation, the container and the dust compact are slowly rotated and driven against a stationary scraper blade by an electrically-operated mechanism. The blade continuously removes dust from the compact surface at a uniform rate. Compressed air enters the container and entrains the dust particles. The dust holder advance rate may be varied by changing the gears in the drive mechanism to provide a wide range of dust concentrations.

A short distance downstream of the dust feeder there is an auxiliary port for introducing additional air for further dilution of the dust cloud. Normally, a flow of 30 liters per minute is passed through the dust feeder itself, and dilution air is added at the rate of 70 liters per minute. Air flow rates are read from calibrated rotameters. Compressed air is supplied to the apparatus from the house compressed air system. This air is dried by passing it through a silica gel bed and then through a high efficiency fibrous filter and a membrane filter to remove particulate matter.

Since dust particles may accumulate electric charges in the dispersal process, the dispersed dust is passed through a charge neutralizer (Thermo-Systems Incorporated, Model 3045) before it is introduced into the dust chamber. The active element of the neutralizer is a 10 millicurie krypton-85 beta source. Beta rays from the krypton-85 interact with air molecules to generate both positive and negative ions. The ions become attached to the dust particles of opposite charge.

The dust chamber itself was constructed from two stainless steel stock pots. The pots are held together by three latches. An O-ring is used to provide an air-tight seal between the two pots. The chamber diameter is 14 inches and its height is 32 inches. Baffles were placed at the entrance and exit of the dust chamber to promote uniform distribution of the aerosol. The baffles are 5.75 inches in diameter, 0.015 inches thick, and are located approximately 1.5 inches away from the exit and entrance ports. The dust chamber is normally operated at a slight positive pressure with respect to the atmosphere (about 2 inches of H_2O). Effluent from the dust chamber is vented to a hood through a one-inch rubber hose.

Twelve sampling ports are located around the periphery of the dust chamber. The filter cassettes are mounted on the inside perimeter of the chamber, and sample flow rate is controlled by critical orifices which are mounted outside the chamber on a U-shaped vacuum line (see Figure 2). The sampling rate is approximately 1.7 liters per minute.

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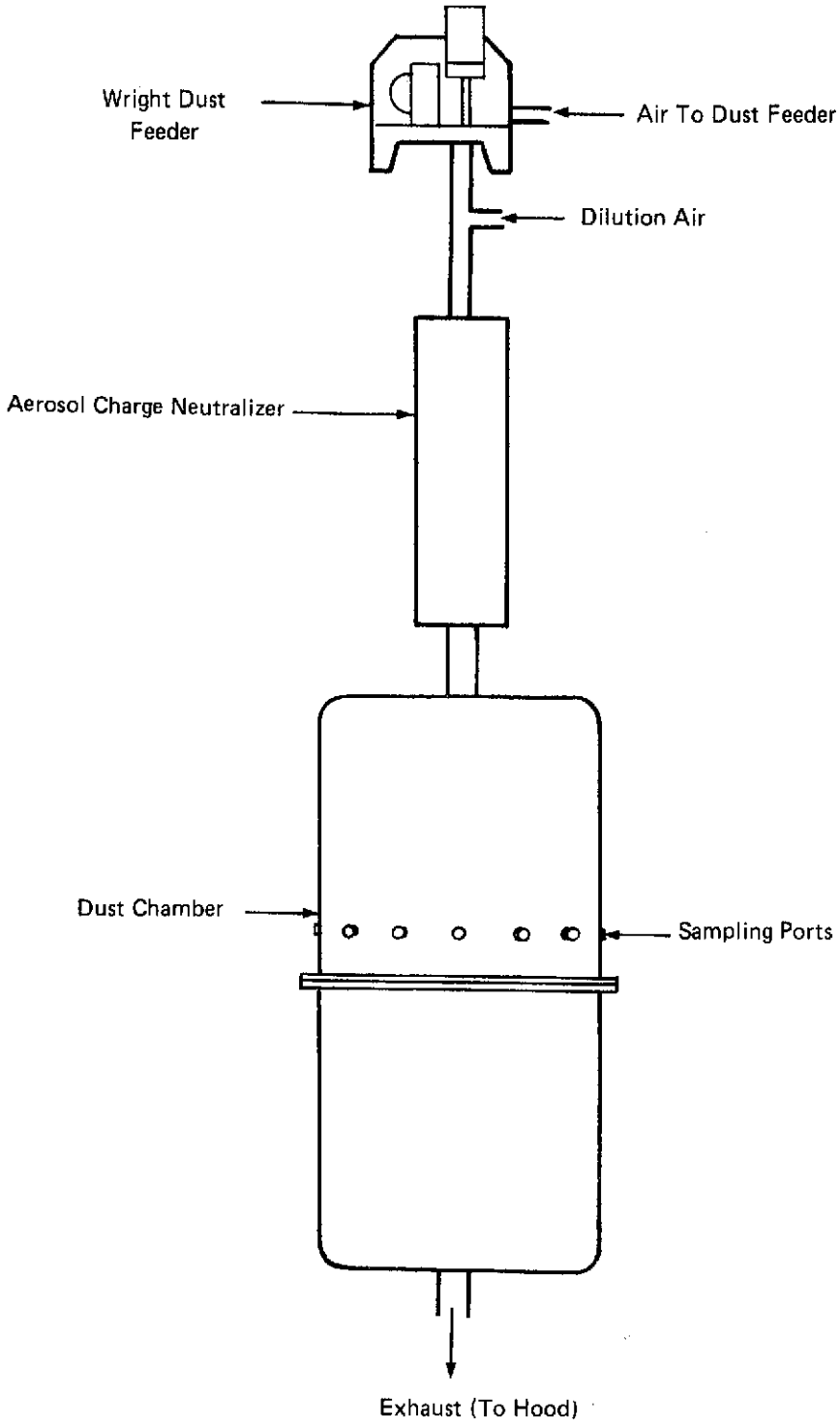

FIGURE 1 DUST GENERATION APPARATUS

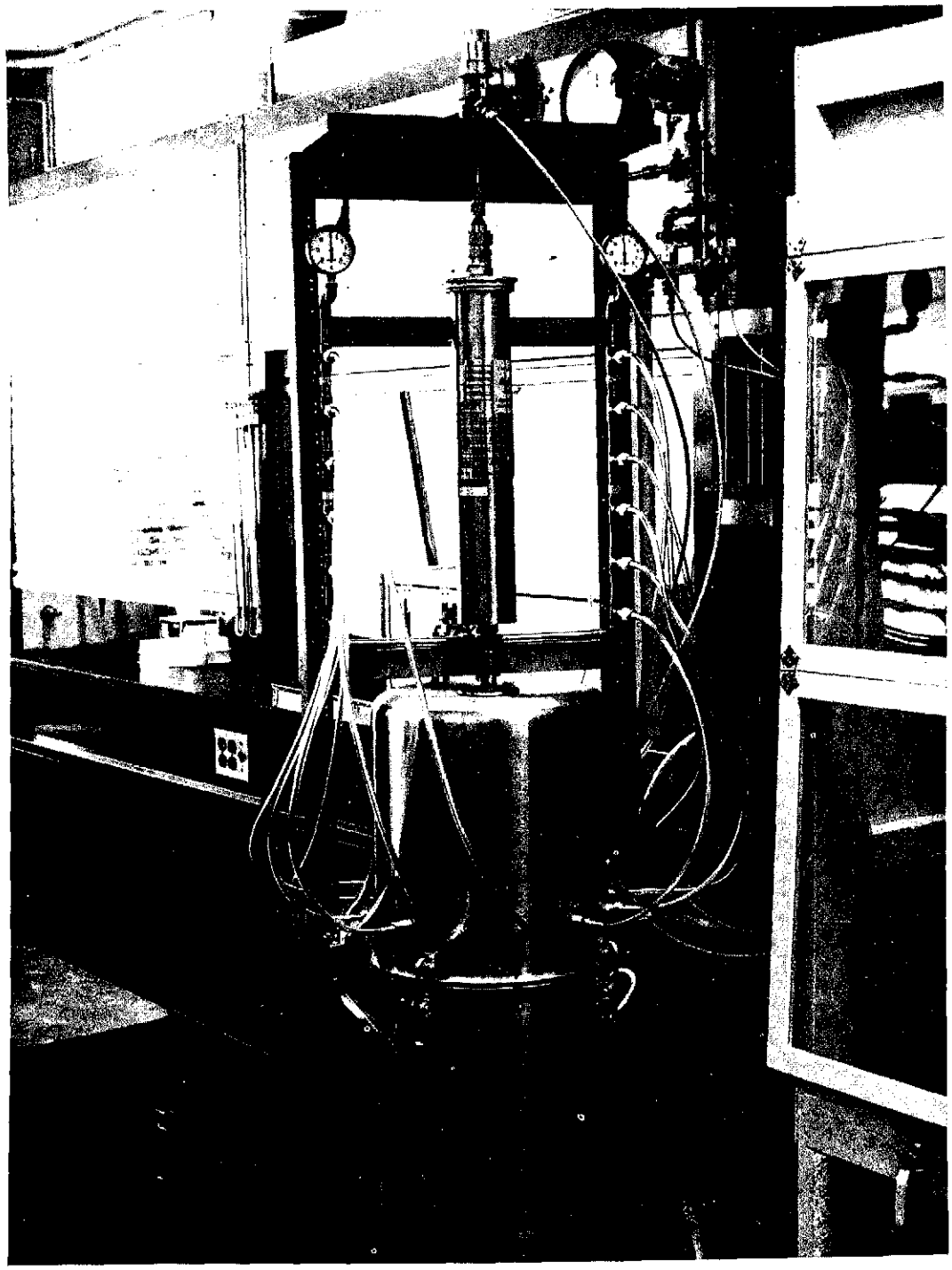

FIGURE 2 PHOTOGRAPH OF DUST GENERATION APPARATUS

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Backup Data Report

Substance: Chloroform, No. S351

OSHA Standard: 240 mg/cu m (Ceiling)

Chemical used for validation: Chloroform, Fisher Chemicals, Spectroquality

Procedure

The general procedure used is described in NIOSH Method No. S351 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of chloroform represented in a 15-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 47.5 mg/min of chloroform via a syringe injector to a dry air stream flowing at a rate of 0.1000 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2400, 0.4990 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 1.1 liters per minute for 15 minutes (17 liters). The generator concentration was also determined using M^3 for calibration as described in the Propane, S87, Backup Data Report. The generator concentration determined from the total hydrocarbon data--99.8, 207.6, and 416 mg/cu m-- was used as the primary basis for the generator concentration. Some leakage at the syringe end accounts for the higher value of generator concentration based on the syringe delivery rate and dilution air ratio. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Note that the data reported includes a set of freshly collected samples and a set stored for 8 days in order to test sample stability and migration. The data obtained showed no migration effects, and no real difference (beyond the normally observed experimental variations) between the fresh and stored samples.

Breakthrough

The first section of the charcoal tube was found to hold 22 mg of chloroform when a test atmosphere containing 485 mg/cu m of chloroform in air was sampled at 0.19 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

In addition, the backup sections of the 17-liter samples collected at 1.1 liters per minute at 2X the OSHA standard level were also analyzed. No trace of chloroform was found in any of the 6 backup tubes analyzed indicating that the collection efficiency is 100%.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0469 \qquad \overline{CV}_2 = 0.0182 \qquad \overline{CV}_T = 0.057$$

The average recovery of the generated samples over all levels was

$$101.3 \pm 9.0\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Chloroform, S351

Analysis

Level	0.5S			1S			2S		
	mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
	1.776	1.948	1.097	3.55	3.24	0.913	7.40	7.14	0.965
	1.776	1.747	0.984	3.55	3.47	0.977	7.40	7.13	0.964
	1.776	1.697	0.956	3.55	3.41	0.961	7.40	7.42	1.003
	1.776	1.590	0.895	3.55	3.30	0.930	7.40	7.21	0.974
	1.776	1.668	0.939	3.55	3.39	0.955	7.40	7.22	0.976
	1.776	1.826	1.028	3.55	3.54	0.997	7.40	7.39	0.999
n =		6			6			6	
mean		0.983			0.956			0.980	
std dev		0.0713			0.0306			0.0169	
CV_1		0.0726			0.0320			0.0172	

$\overline{CV}_1$ 0.0469

$\overline{CV}_{A+\overline{DE}}$ 0.0506

Data Sheet: Chloroform, S351

Sampling and Analysis
(Sample Stored for 8 Days)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.599	1.643	17.00	96.7	99.8	
	1.629	1.674	16.73	100.1	99.8	
	1.591	1.635	16.73	97.7	99.8	
	1.609	1.654	16.97	97.4	99.8	
	1.606	1.651	16.86	97.9	99.8	
	1.594	1.638	16.76	97.7	99.8	
			n = 6			
			mean	97.9		98.1
			std dev	1.150		
			CV_2	0.0117		
1S	3.61	3.71	16.89	219.7	207.6	
	3.54	3.64	16.98	214.4	207.6	
	3.48	3.58	17.19	208.3	207.6	
	3.48	3.58	17.03	210.2	207.6	
	3.34	3.43	16.88	203.2	207.6	
	3.41	3.51	16.89	207.8	207.6	
			n = 6			
			mean	210.6		101.5
			std dev	5.75		
			CV_2	0.0273		
2S	7.13	7.33	16.66	440	416	
	7.06	7.26	16.62	437	416	
	7.17	7.37	16.85	437	416	
	7.15	7.35	16.92	434	416	
	7.03	7.23	16.91	428	416	
	7.00	7.19	16.73	430	416	
			n = 6			
			mean	434		104.3
			std dev	4.59		
			CV_2	0.0106		
			$\overline{CV}_2$	0.0182		

Data Sheet: Chloroform, S351

Sampling and Analysis
(Sample Stored 1 Day)

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.336	1.373	16.93	81.1	92.2	
	1.359	1.397	16.66	83.9	92.2	
	1.474	1.515	16.66	90.9	92.2	
	1.333	1.370	16.90	81.1	92.2	
	1.358	1.396	16.80	83.1	92.2	
	1.333	1.370	16.72	81.9	92.2	
			n = 6			
			mean	83.7		90.8
			std dev	3.71		
			CV_2	0.0444		
1S	2.861	2.940	16.83	174.7	187.6	
	2.787	2.864	16.92	169.3	187.6	
	2.842	2.921	17.13	170.5	187.6	
	2.772	2.849	16.96	168.0	187.6	
	2.453	2.521	16.81	150.0	187.6	
	2.585	2.657	16.83	157.9	187.6	
			n = 6			
			mean	165.1		88.0
			std dev	9.24		
			CV_2	0.0560		
2S	4.03	4.14	16.60	249*	374	
	5.57	5.72	16.55	346	374	
	5.62	5.78	16.78	344	374	
	5.60	5.76	16.86	342	374	
	5.58	5.73	16.84	340	374	
	5.77	5.93	16.66	360	374	
			n = 5			
			mean	346		92.5
			std dev	7.92		
			CV_2	0.0229		
			$\overline{CV_2}$	0.0444		

*These values excluded from statistical analysis.

Backup Data Report

Substance:	Chromium, Metal and Insoluble Compounds, No. S352	
OSHA Standard:	1 mg/cu m	
Chemical Used for Validation:	Analytical:	Chromium Metal
	Generation:	Chromium Hexacarbonyl

Procedure

The general procedure for collecting and measuring concentrations of the analyte in air is described in NIOSH Method S352, which has been adapted from P&CAM 173. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 90-liter sample at 0.5X, 1X, and 2X the OSHA standard. Accurately weighed but appropriate amounts (45, 90, and 180 μg) of 100-mesh chromium metal were added to 37-mm/0.8-micron type AA MCEF filters. The filters were digested in 6 M hydrochloric acid to solubilize the chromium metal and concentrated nitric acid to destroy the filters and any other organic material. The digested sample was then dissolved in 1 ml concentrated nitric acid and diluted to 20 ml with deionized water prior to AA analysis. The results of the analytical work are given in the Analysis Table at the end of this report. Analyses were done on a Varian Techtron AA6 atomic absorption spectrophotometer. The absorbance, measured at 357.9 nm, was used as a measure of the chromium concentration in the sample. This procedure was used for the analysis of 18 generated samples, six at each of three standard levels. Details of the analytical procedure may be found in Section 8.4 of NIOSH Method No. S352. Details of the generation of the analyte at three concentration levels of approximately 0.5, 1, and 2 times the OSHA standard are given below.

Modifications

A major modification of P&CAM 173 was the use of both 6 M HCl and concentrated HNO_3 in the digestion process. It was found that concentrated HNO_3 did not sufficiently solubilize the insoluble chromium compounds, thus necessitating the use of equal volumes of 6 M HCl and concentrated HNO_3.

Another modification of P&CAM 173 was the use of a reducing nitrous oxide acetylene flame instead of a reducing air acetylene flame.

Generation

Samples were generated using chromium hexacarbonyl as the starting material. The hexacarbonyl was chosen because it is known to thermally decompose at 135°C and because it has a significant vapor pressure. The design of the generation system is shown in Figure 1.

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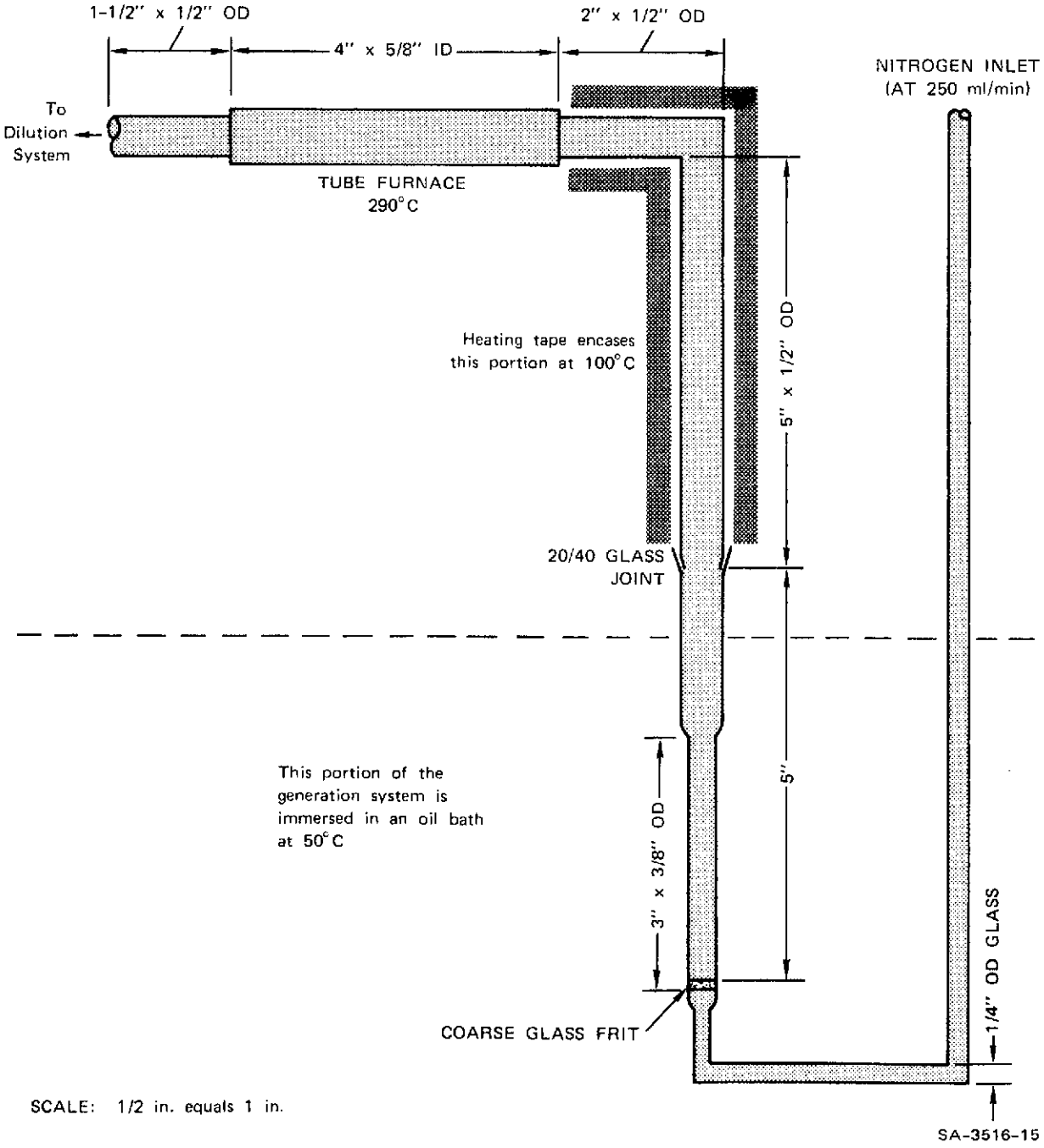

FIGURE 1 SCHEMATIC OF THE GENERATION SYSTEM FOR CHROMIUM METAL AND INSOLUBLE COMPOUNDS

Approximately one gram of chromium hexacarbonyl was placed in the generator on top of the coarse glass frit. The generator was assembled and connected to the dilution system. The portion of the generator containing the chromium hexacarbonyl was immersed in an oil bath thermostated at 50°C. The temperature of the heating tape was adjusted to 100°C, and the oven was heated to 290°C. Nitrogen was introduced into the system at a flow rate of 250 ml/min. Chromium hexacarbonyl has a vapor pressure of 2.88 mm at 50°C [derived from log P(mm) = 10.63-3285/T (°K)] and is easily volatilized and swept into the oven by the nitrogen stream. Condensation of the hexacarbonyl vapor in the generator prior to the oven is prevented by maintaining the area at an elevated temperature with a heating tape. The material leaving the oven then enters the dilution system, which is described in Reference No. 1.

Prior to sample collection, it was necessary to determine the amount of dilution air needed to dilute the generator output to produce the desired concentration levels. To do this, a known amount of air was added, then several samples were collected and analyzed. The results of this test were used to select the correct amount of dilution air to give approximately the 2X OSHA standard level.

The output of the generator was diluted with air at a rate of 10 liters/min, 20 liters/min, and 40 liters/min to give approximately the 2X, 1X, and 0.5X OSHA standard levels, respectively.

Several characterization tests were performed on the generated material. The material collected on the filter was not water soluble. X-ray diffraction analysis indicated the presence of chromium nitride. Scanning electron micrographs show that the particles are entirely submicron (0.044-0.067 micron).

Collection Efficiency

Collection efficiency at a concentration of 1.830 mg/cu m was determined by measuring the amount of particulate collected on each of the two filters in series mounted in direct contact with each other. The collection efficiency of the filter was found to be 1.00 at a detection limit of 0.012 mg/cu m. Thus, no correction for collection efficiency is needed in this method.

mg/cu m found first filter	mg/cu m found second filter	Collection Efficiency
1.842	N.D.*	1.00
1.764	"	1.00
1.993	"	1.00
1.842	"	1.00
1.742	"	1.00
1.800	"	1.00

* N.D. = Not detected at a detection limit of 0.012 mg/cu m.

Discussion

At the outset of work, three different wet-ashing techniques were attempted to effect solubilization of the insoluble chromium compound and chromium metal. These techniques involved the use of a single acid during the wet-ashing procedure. One 37-mm/0.8-micron type AA MCEF filter was added to each clean 100-ml beaker. The amount of chromium metal that would be collected in a 90 liter sample at 1X the OSHA standard (90 μg) was placed in the beaker on top of the filter. One-third of the samples were digested with three 2-ml portions of 6 M hydrochloric acid on a hot plate set at 140°C. One third of the samples were digested with three 2-ml portions of concentrated nitric acid. The final third of the samples were digested in concentrated perchloric acid. After digestion, the residue was dissolved in 1 ml concentrated nitric acid. The sample was diluted to 20 ml and then subjected to AA analysis.

Sample digestion with concentrated perchloric acid showed recoveries of less than 5%. Concentrated nitric acid digestion showed a recovery of less than 50%.

A two-step digestion process was attempted. A primary digestion with 6 M hydrochloric acid was followed by digestion in concentrated nitric acid. Preliminary work showed that at the 1X OSHA level recoveries were approximately 92%.

The details of the analysis procedure is described in Section 8.4 of NIOSH Method No. S352.

Precision and Accuracy

The statistical procedures used are described in Reference No. 2.

$\overline{CV}_1 = 0.059$ $\overline{CV}_2 = 0.052$ $\overline{CV}_T = 0.076$

Data Sheet: Chromium, Metal and Insoluble Salts S352

Analysis (Cr metal)

Level	0.5S		1S			2S		
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
48.4	49.0	1.012	87.2	88.0	1.009	187.2	172.0	0.919
40.8	37.0	0.907	90.0	82.0	0.911	191.6	182.0	0.950
56.4	56.0	0.993	85.6	80.0	0.935	185.8	202.0	1.087
50.2	54.0	1.076	93.6	86.0	0.919	185.4	188.0	1.014
42.2	40.0	0.948	95.2	86.0	0.903	184.0	200.0	1.087
43.6	43.0	0.986	100.2	100.0	0.998	180.2	178.0	0.988
n =		6			6			6
mean		0.987			0.946			1.008
std dev		0.057			0.046			0.070
CV_1		0.058			0.049			0.069

$\overline{CV}_1$ 0.059

$\overline{CV}_{A+\overline{AMR}}$ 0.064

Data Sheet: Chromium Metal and Insoluble Salts S352

Sampling and Analysis (Chromium Nitride)

Test Level	---------- Found ----------		
	µg	Liters	mg/cu m*
0.5S	45.7	88.9	0.514
	43.1	92.2	0.467
	43.7	84.2	0.519
	41.8	90.0	0.464
	42.4	91.1	0.465
	47.0	88.9	0.529
		n = 6	
		mean	0.493
		std dev	0.031
		CV_2	0.063
1S	76.8	88.9	0.864
	78.1	92.2	0.847
	75.6	84.2	0.898
	73.0	90.0	0.811
	73.6	91.1	0.808
	72.3	88.9	0.813
		n = 6	
		mean	0.840
		std dev	0.036
		CV_2	0.043
2S	163.8	88.9	1.842
	162.6	92.2	1.764
	167.8	84.2	1.993
	165.8	90.0	1.842
	158.7	91.1	1.742
	160.0	88.9	1.800
		n = 6	
		mean	1.830
		std dev	0.089
$\overline{CV}_2$ 0.052		CV_2	0.049

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

4. Udy, Marvin, Chromium, Vol. 1, "Chemistry of Chromium and Its Compounds," ACS Monograph Series, Reinhold Publishing, 1956.

Backup Data Report

Substance: Dichloroethyl Ether, No. S357

OSHA Standard: 15 ppm (90 mg/cu m) - Ceiling

Chemical Used for Validation: Dichloroethyl Ether
Aldrich

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of dichloroethyl ether in air is described in NIOSH Method S357, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2X, 1X, and 0.5X the OSHA standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of dichloroethyl ether to represent 15-liter air samples. Samples of dichloroethyl ether in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of dichloroethyl ether in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 15 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined from the delivery rate of the syringe drive pump and the dilution air flow rates. The total hydrocarbon analyzer, calibrated with bag standards, was used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

A hexane solution of dichloroethyl ether containing 0.337 g/ml was used to apply the analyte onto the charcoal for the desorption efficiency tests so that it would not be necessary to inject less than two microliters at the 0.5X OSHA standard level.

Generation

Samples of dichloroethyl ether were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-inch long stainless steel needle was attached to the syringe. The needle passed through a rubber septum with the end in a heated glass tube. The syringe drive pump

delivered the analyte at a rate of 7.85 microliters/minute into the tube which was packed with glass wool. The vapor was carried out of the first stage of the generator by a stream of nitrogen at a flow rate of 7.28 liters/minute and diluted with air at a rate of 45.9 liters/minute to obtain the 2X OSHA standard level. Additional dilutions were made to obtain the 1X and 0.5X OSHA standard levels. The dilution system is described in Reference No. 1. The concentrations in the three chambers were monitored during sampling with a hydrocarbon analyzer, calibrated with bag standards.

Samples were collected for 15 minutes at a rate of approximately 1.0 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The two-piece vapor generator described in Reference No. 3 was used. The following generating conditions were used in the breakthrough test:

Nitrogen flow rate: 1.30 liters/minute at 20°C
Dilution air flow rate: 31.1 liters/minute at 20°C

A total hydrocarbon analyzer was used to monitor the concentration during the test. Breakthrough, 5% of the generated concentration of 161 mg/cu m in the effluent, was observed after 115.3 minutes of sampling at a rate of 0.90 liter per minute. The test was continued until after a total sampling time of four hours.

Discussion

A time study on dichloroethyl ether was conducted at 1X the OSHA standard level by spiking 100-mg portions of charcoal Lot 105 with 4 microliters of a solution of dichloroethyl ether in hexane containing 0.337 g/ml. A hydrogen flame ionization gas chromatographic method was used in the study. The GC conditions are given below:

1. 50 ml/min nitrogen carrier gas flow
2. 65 ml/min hydrogen gas flow to detector
3. 500 ml/min air flow to detector
4. 225°C injector temperature
5. 275°C manifold temperature (detector)
6. 135°C column temperature

A stainless steel column (10-ft long X 1/8-in O.D.) packed with 10% FFAP on 80/100 mesh Chromosorb W DMCS was used. The samples were allowed to stand for one week before analysis. The samples were desorbed with carbon disulfide. The time study results were compared with the 1X D.E. data at the end of this report which represents samples which were analyzed immediately. It was concluded that

dichloroethyl ether was stable on charcoal for at least one week.

TIME STUDY OF DICHLOROETHYL ETHER

mg taken	mg found		Recovery
1.348	1.222		0.907
1.348	1.223		0.907
1.348	1.232		0.914
1.348	1.236		0.917
1.348	1.241		0.921
1.348	1.249		0.927
		mean	0.916
		std dev	0.008
		CV	0.009

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$\overline{CV}_1 = 0.007$ $\overline{CV}_2 = 0.032$ $\overline{CV}_T = 0.059$

The average recovery at the OSHA standard level was 90.7%.

It was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. The low recoveries at the three levels were attributed to equipment problems and probably do not represent a bias. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Dichloroethyl Ether S357

Analysis

Level	0.5S		1S			2S		
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
0.674	0.620	0.920	1.348	1.278	0.948	2.70	2.54	0.941
0.674	0.613	0.909	1.348	1.274	0.945	2.70	2.57	0.952
0.674	0.620	0.920	1.348	1.286	0.954	2.70	2.58	0.956
0.674	0.621	0.921	1.348	1.286	0.954	2.70	2.59	0.959
0.674	0.607	0.901	1.348	1.286	0.954	2.70	2.58	0.956
0.674	0.624	0.926	1.348	1.294	0.960	2.70	2.58	0.956
n =		6			6			6
mean		0.916			0.952			0.953
std dev		0.009			0.005			0.006
CV_1		0.010			0.005			0.006

$\overline{CV}_1$ 0.007

$\overline{CV}_{A+\overline{DE}}$ 0.008

A hand drawn curve was used to calculate the corr. mg in the Sampling and Analysis table.

Data Sheet: Dichloroethyl Ether S357

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery (%)
0.5S	0.518	0.577	13.73	42.0	45.0	
	0.494	0.552	13.58	40.6	45.0	
	0.530	0.589	14.07	41.9	45.0	
	0.497	0.555	13.56	40.9	45.0	
	0.552	0.611	14.45	42.3	45.0	
	0.550	0.608	14.52	41.9	45.0	
			n = 6			
			mean	41.6		92.4
			std dev	0.7		
			CV_2	0.017		
1S	0.932	1.002	12.23	81.9	90.0	
	0.986	1.057	12.93	81.8	90.0	
	1.053	1.123	13.53	83.0	90.0	
	0.999	1.070	13.64	78.5	90.0	
	1.034	1.105	13.44	82.2	90.0	
	1.045	1.115	13.62	81.9	90.0	
			n = 6			
			mean	81.6		90.7
			std dev	1.6		
			CV_2	0.020		
2S	2.005	2.104	13.85	151.9	180.0	
	2.186	2.289	13.05	175.4	180.0	
	2.132	2.239	13.46	166.3	180.0	
	2.308	2.412	14.09	171.2	180.0	
	2.314	2.418	14.43	167.6	180.0	
	2.340	2.443	14.40	169.7	180.0	
			n = 6			
			mean	167.0		92.8
			std dev	8.1		
$\overline{CV}_2$ 0.032			CV_2	0.048		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Backup Data Report, Epichlorohydrin, No. S118, prepared under NIOSH Contract CDC-99-74-45.

4. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, Ed., p. 387, (University of California Press, Los Angeles, California, 1973).

6. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance:	Diisobutyl Ketone, No. S358
OSHA Standard:	50 ppm (290 mg/cu m)
Chemical Used for Validation:	Diisobutyl Ketone Chemical Samples Company

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of diisobutyl ketone in air is described in NIOSH Method S358, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA standard by spiking 100-mg portions of charcoal Lot 105 with the appropriate amounts of diisobutyl ketone to represent 12-liter air samples. Samples of diisobutyl ketone in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of diisobutyl ketone in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 63.2 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined using bag standards and a total hydrocarbon analyzer. The total hydrocarbon analyzer was also used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were no major modifications to P&CAM 127.

Generation

Samples of diisobutyl ketone were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-in long stainless steel needle was attached to the syringe. The needle passed through a rubber septum with the end in a heated glass tube. The syringe drive pump delivered the analyte into the tube which was packed with glass wool. The vapor was carried out of the first stage of the generator by a stream of nitrogen and diluted with air downstream from the heated zone to obtain the 2X OSHA level. Additional dilutions were made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The concentration of the 2X chamber was monitored during sampling with a hydrocarbon analyzer.

The concentration in the 2X, 1X, and 0.5X sampling chambers were determined by using bag standards and comparing the bag standard response with the chamber responses on the total hydrocarbon analyzer. Samples were collected for 63.2 minutes at a rate of approximately 0.20 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test. Breakthrough, 5% of the generated concentration of 582 mg/cu m in the effluent, was observed after 219 minutes of sampling at a rate of 0.20 liter per minute at which time the test was discontinued.

Discussion

A time study on diisobutyl ketone was conducted at 1X the OSHA standard level by spiking 100-mg portions of charcoal Lot 105 with 3.46 mg of diisobutyl ketone. A hydrogen flame ionization gas chromatographic method was used in the study. The GC conditions are given below:

1. 50 ml/min nitrogen carrier gas flow
2. 65 ml/min hydrogen gas flow to detector
3. 500 ml/min air flow to detector
4. 230°C injector temperature
5. 241°C manifold temperature
6. 71°C column temperature

A stainless steel column (10-ft X 1/8-in.) packed with 10% FFAP on 80/100 mesh Chromosorb W DMCS was used.

The samples were allowed to stand for one week before analysis. The samples were desorbed with carbon disulfide. The results given on the next page support the conclusion that diisobutyl ketone is stable on charcoal for at least one week. These results were compared with results in the Analysis table at the end of this report, which represents samples which were immediately analyzed.

TIME STUDY OF DIISOBUTYL KETONE

mg taken	mg found	D.E.
3.46	3.26	0.942
3.46	3.11	0.899
3.46	3.40	0.983
3.46	3.48	1.006
3.46	3.57	1.032
3.46	3.34	0.965
	mean	0.971
	std dev	0.047
	CV	0.048

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.032$ $\overline{CV}_2 = 0.047$ $\overline{CV}_T = 0.070$

The average recovery at the OSHA standard level was 98.6%.

It was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. The 2X data meet the statistical criteria of the program. The lower recovery and poorer reproducibility were attributed to equipment problems and probably do not represent a bias. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Diisobutyl Ketone S358

Analysis

Level	0.5X			1X			2X	
taken	found	DE	taken	found	DE	taken	found	DE
1.771	1.679	0.948	3.46	3.44	0.994	7.00	6.86	0.980
1.771	1.696	0.958	3.46	3.48	1.006	7.00	7.08	1.011
1.771	1.643	0.928	3.46	3.21	0.928	7.00	6.83	0.976
1.771	1.639	0.925	3.46	3.52	1.017	7.00	6.27	0.896
1.771	1.696	0.958	3.46	3.33	0.962	7.00	6.83	0.976
1.771	1.630	0.920	3.46	3.49	1.009	7.00	6.84	0.977

n =	6	6	6
mean	0.940	0.986	0.969
std dev	0.017	0.034	0.038
CV_1	0.018	0.034	0.039

$\overline{CV}_1$ 0.032

$\overline{CV}_{A+\overline{DE}}$ 0.035

The equation D.E. = $0.974 - e^{-2.008 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Diisobutyl Ketone S358

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m*	mg/cu m	Recovery (%)
0.5S	1.735	1.840	12.19	150.9	145.5	
	1.771	1.874	13.14	142.6	145.5	
	1.671	1.780	12.07	147.5	145.5	
	1.721	1.827	12.38	147.6	145.5	
	1.752	1.856	12.76	145.4	145.5	
	1.668	1.778	12.19	145.9	145.5	
			n = 6			
			mean	146.6		100.8
			std dev	2.8		
			CV_2	0.019		
1S	2.86	2.95	11.18	264	291	
	3.18	3.27	11.25	291	291	
	3.34	3.43	11.44	300	291	
	3.06	3.15	10.87	290	291	
	2.82	2.91	9.92	293	291	
	3.08	3.17	11.12	285	291	
			n = 6			
			mean	287		98.6
			std dev	12		
			CV_2	0.042		
2S	6.71	6.89	12.70	543	582	
	6.76	6.94	12.51	555	582	
	6.26	6.43	11.88	541	582	
	5.66	5.81	11.94	487	582	
	6.65	6.82	11.44	596	582	
	Sample was lost.					
			n = 5			
			mean	544		93.5
			std dev	39		
$\overline{CV}_2$ 0.047			CV_2	0.072		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Dioxane

OSHA Standard: 360 mg/cu m

Chemical used for
validation: p-Dioxane, Eastman Reagent

Procedure

The general procedure used is described in NIOSH Method No. S360 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of dioxane represented in a 10-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this auto-sampler using decane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 66.4 mg/min of dioxane via a syringe injector to a dry air stream flowing at a rate of 0.1020 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 44 minutes (10 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 26 mg of dioxane when a test atmosphere containing 651 mg/cu m of dioxane in air was sampled at 0.19 liters per minute for 210 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

1212<

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0174 \qquad \overline{CV}_2 = 0.0202 \qquad \overline{CV}_T = 0.0544$$

The average recovery of the generated samples over all levels was

$$108.9 \pm 6.7\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: p-Dioxane S360

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
1.812	1.578	0.871	3.62	3.31	0.914	7.25	6.39	0.881
1.812	1.625	0.897	3.62	3.27	0.903	7.25	6.28	0.866
1.812	1.588	0.876	3.62	3.31	0.914	7.25	6.19	0.854
1.812	1.570	0.866	3.62	3.16	0.873	7.25	6.29	0.868
1.812	1.571	0.867	3.62	3.24	0.895	7.25	6.25	0.862
1.812	1.585	0.875	3.62	3.11	0.859	7.25	6.28	0.866
n =		6			6			6
mean		0.875			0.893			0.866
std dev		0.0114			0.0225			0.0088
CV_1		0.0130			0.0252			0.0102

$\overline{CV_1}$ 0.0174

$\overline{CV_{A+\overline{DE}}}$ 0.0188

Data Sheet: p-Dioxane S360
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.560	1.781	9.70	183.6	157.3	
	1.447	1.656	9.70	170.7	157.3	
	1.453	1.662	9.70	171.3	157.3	
	1.426	1.633	9.70	168.4	157.3	
	1.471	1.683	9.70	173.5	157.3	
	1.467	1.678	9.70	173.0	157.3	
			n = 6			
			mean	173.4		110.2
			std dev	5.31		
			CV_2	0.0306		
1S	3.01	3.37	9.70	347	324	
	3.03	3.40	9.62	353	324	
	2.89	3.24	9.53	340	324	
	3.07	3.44	9.87	349	324	
	3.03	3.40	9.75	349	324	
	3.02	3.39	9.66	351	324	
			n = 6			
			mean	348		107.4
			std dev	4.49		
			CV_2	0.0129		
2S	6.29	7.26	10.00	726	660	
	6.04	6.93	9.75	711	660	
	6.17	7.10	9.75	728	660	
	6.08	6.98	9.70	720	660	
	6.34	7.33	10.10	726	660	
	6.03	6.92	9.75	710	660	
			n = 6			
			mean	720		109.1
			std dev	7.96		
			CV_2	0.0111		
			$\overline{CV}_2$	0.0202		

1215<

Backup Data Report

Substance:	Isophorone, No. S367
OSHA Standard:	25 ppm (140 mg/cu m)
Chemical Used for Validation:	Isophorone Aldrich

Procedure

The procedure followed for validation of the method for collecting and measuring concentrations of isophorone in air is described in NIOSH Method S367, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 2, 1, and 0.5 times the OSHA standard by spiking 100-mg portions of charcoal Lot 104 with the appropriate amounts of isophorone to represent 12-liter air samples. Samples of isophorone in air were generated and collected on petroleum-based charcoal, Lot 104, supplied by SKC, Inc., Pittsburgh, Pa. The samples were desorbed with carbon disulfide and analyzed by gas chromatography. The amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of isophorone in air were determined by dividing the corrected mg found by the sampled volume (critical orifice flow rate for that sample X 60.8 minutes). The "true" concentration at 2X, 1X, and 0.5X the OSHA standard levels were determined using bag standards and a total hydrocarbon analyzer. The total hydrocarbon analyzer was also used to monitor the stability of the concentrations in the three sampling chambers during sampling.

Modifications

There were two major modifications to P&CAM 127.

1. The analyte was collected on petroleum-based charcoal Lot 104 instead of activated coconut charcoal Lot 105. The reason for this modification is given in the Discussion Section of this report.

2. A solution of isophorone in hexane (424.6 µg/µl) was used to apply the analyte to the charcoal for desorption efficiency tests, so it would not be necessary to inject less than 2 µl at the 0.5X level.

Generation

Samples of isophorone were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-in. long stainless steel needle was attached to the syringe. The needle passed through a rubber septum with the end in a glass tube which was heated with a heating lamp. The syringe drive pump delivered the analyte into the tube which was packed with glass

wool. The vapor was carried out of the first stage of the generator by a stream of nitrogen and diluted with air downstream from the heated zone to obtain 2X the OSHA level. Additional dilutions were made to obtain the 1X and 0.5X OSHA levels. The dilution system is described in Reference No. 1. The concentration of the 2X chamber was monitored during sampling with a hydrocarbon analyzer.

The concentrations in the 2X, 1X, and 0.5X sampling chambers were determined by using bag standards and comparing the bag standard response with the chamber responses on the total hydrocarbon analyzer. Samples were collected for 60.8 minutes at a rate of approximately 0.19 liter per minute (individual dritical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tube was conducted as described in Reference No. 2. The conditions described above were used. A total hydrocarbon analyzer was used to monitor the concentration during the breakthrough test. Less than 5% of the generated concentration of 283 mg/cu m in the effluent was observed after 240 minutes of sampling at a rate of 0.19 liter per minute, at which time the test was discontinued. Breakthrough was not observed.

Discussion

A time study on isophorone was conducted at 1X the OSHA standard level by spiking 100-mg portions of charcoal Lot 104 with 4 µl of a hexane solution of isophorone containing 424.6 µg/µl. A hydrogen flame ionization gas chromatographic method was used in the study. The GC conditions are given below:

1. 50 ml/min nitrogen carrier gas flow
2. 65 ml/min hydrogen gas flow to detector
3. 500 ml/min air flow to detector
4. 255°C injector temperature
5. 250°C manifold temperature
6. 167°C column temperature

A stainless steel column (10-ft X 1/8-in.) packed with 10% FFAP on 80/100 mesh Chromosorb W DMCS was used.

The samples were allowed to stand for one week before analysis. The samples were desorbed with carbon disulfide. The results given on the next page support the conclusion that isophorone is stable on charcoal

for at least one week. The time study results were compared with the 1X D.E.'s in the Analysis Table at the end of this report. The data in the Analysis Table represent samples which were analyzed immediately.

TIME STUDY RESULTS OF ISOPHORONE

mg taken	mg found	DE
1.698	1.421	0.837
1.698	1.432	0.843
1.698	1.416	0.834
1.698	1.402	0.826
1.698	1.424	0.839
1.698	1.387	0.817
	n = 6	
	mean	0.833
	std dev	0.010

Preliminary desorption efficiency tests were conducted on charcoal Lot 105 and Lot 104 at 1X the OSHA standard for a 12-liter sample. Four microliters of a solution of isophorone in hexane (424.6 μg/μl) were used to spike both lots of charcoal. Carbon disulfide, methanol and acetone were tested as possible desorbing solvents. The samples were allowed to stand for 30 minutes in 1 ml of desorbing solvent, and analyzed by GC. The results are presented below:

	Desorbing Solvent	D.E.
Charcoal Lot 105	Carbon disulfide	0.740
Charcoal Lot 105	Methanol	0.198
Charcoal Lot 105	Acetone	0.706
Charcoal Lot 104	Carbon disulfide	0.860

From the above results, charcoal Lot 104 was chosen as the solid sorbent, and carbon disulfide as the desorbing solvent.

Precision and Accuracy

The statistical procedures used are described in Reference No. 3.

$\overline{CV}_1 = 0.033$ $\overline{CV}_2 = 0.026$ $\overline{CV}_T = 0.058$

The average recovery at the OSHA standard level was 105%.

However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, it was concluded that any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, $\overline{CV}_T$ is a measure of accuracy as well as precision of the sampling and analytical method.

Data Sheet: Isophorone S367

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
0.849	0.691	0.814	1.698	1.487	0.876	3.40	2.85	0.838
0.849	0.709	0.835	1.698	1.484	0.874	3.40	3.00	0.882
0.849	0.755	0.889	1.698	1.437	0.846	3.40	3.07	0.903
0.849	0.715	0.842	1.698	1.454	0.856	3.40	3.06	0.900
0.849	0.745	0.878	1.698	1.435	0.845	3.40	2.75	0.809
0.849	0.710	0.836	1.698	1.461	0.860	3.40	3.01	0.885
n =		6			6			6
mean		0.849			0.860			0.870
std dev		0.029			0.013			0.038
CV_1		0.034			0.015			0.044

$\overline{CV}_1$ 0.033

$\overline{CV}_{A+\overline{DE}}$ 0.036

The equation D.E. = $0.866 - e^{-5.49 \times \text{mg found}}$ was used to calculate the corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference No. 4.

Data Sheet: Isophorone S367

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery (%)
0.5S	0.681	0.809	11.88	68.1	67.5	
	0.718	0.848	12.21	69.5	67.5	
	0.739	0.870	12.53	69.4	67.5	
	0.624	0.749	11.65	64.3	67.5	
	0.617	0.742	10.35	71.7	67.5	
	0.708	0.838	11.73	71.4	67.5	
			n = 6			
			mean	69.1		102.4
			std dev	2.7		
			CV_2	0.039		
1S	1.329	1.536	10.33	148.7	139.2	
	1.435	1.657	11.39	145.5	139.2	
	1.031	1.195	9.52	125.5*	139.2	
	1.267	1.465	10.31	142.1	139.2	
	1.334	1.542	10.53	146.4	139.2	
	1.400	1.617	10.90	148.4	139.2	
			n = 5			
			mean	146.2		105.0
			std dev	2.7		
			CV_2	0.018		
2S	3.19	3.68	12.16	303	283	
	3.13	3.61	11.87	304	283	
	2.96	3.42	11.27	303	283	
	2.98	3.44	11.27	305	283	
	2.87	3.31	10.66	311	283	
	2.94	3.39	11.27	301	283	
			n = 6			
			mean	304		107.4
			std dev	3		
$\overline{CV}_2$	0.026		CV_2	0.010		

* This value was deleted, because it did not pass the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

References

1. Backup Data Report, Cumene, No. S23, prepared under NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Cyclohexene, No. S82, prepared under NIOSH Contract CDC-99-74-45.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

4. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387 (University of California Press, Los Angeles, California, 1973).

5. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

Backup Data Report

Substance: Isopropyl Ether, No. S368

OSHA Standard: 500 ppm (2100 mg/cu m)

Chemical Used for Validation: iso-Propyl ether, $[(CH_3)_2\ CH]_2O$, Fisher Scientific Company, certified

Procedure

The general procedure used is described in NIOSH Method No. S38 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate amount of isopropyl ether represented in a 3-liter air sample. The sample size recommended is based on 2/3 the volume capacity of 5% breakthrough when a test atmosphere containing the analyte at 2X OSHA standard concentration was sampled at 0.2 liter per minute. The charcoal used was 100 mg of Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Two sets of 18 analytical samples were prepared; one set was stored overnight while the other set was stored for 5 days. The desorption efficiency found for these two sets of samples shown in Tables 1 and 2 were similar (0.937 vs. 0.934) indicating that the samples were stable over the 5-day storage period.

All samples were analyzed in a Varian 2700 gas chromatograph equipped with a flame ionization detector and automatic sample injector. Undecane was used as internal standard. The appropriate DE correction factor used was determined from the "hand drawn" DE curve based on the data from the two sets of analytical samples studied. Details of the analysis procedure may be found in the Butyl Acetate S47 Backup Data Report and Attachment.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 430 mg/min of isopropyl ether via a syringe injector to a dry air stream flowing at a rate of 0.101 cu m/min. The three sample lines were then maintained at dilution ratios of 0.233, 0.486 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.06 liter per minute for 43 minutes (3 liters). A sample size of 3 liters was used on the basis of the two-thirds breakthrough capacity. The data reported is for a set of 18 samples collected and stored for 5 days (Table 3). The backup sections

TABLE 1

Data Sheet: Isopropyl Ether, S368
(Lot 105/100 mg; Samples Stored 1 Day)

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.16	2.980	0.943	6.33	5.87	0.927	12.58	11.49	0.913
3.16	2.940	0.930	6.33	5.93	0.937	12.58	11.27	0.896
3.16	3.003	0.950	6.33	5.93	0.937	12.58	12.26	0.975
3.16	2.995	0.948	6.33	5.88	0.929	12.58	11.74	0.933
3.16	3.003	0.950	6.33	5.82	0.919	12.58	12.12	0.963
3.16	2.964	0.938	6.33	5.81	0.918	12.58	12.11	0.963
n =		6			6			6
mean		0.943			0.928			0.941
std dev		0.00796			0.00830			0.0316
CV_1		0.00844			0.00895			0.0336

$\overline{CV}_1$ 0.0207

$\overline{CV}_{A+\overline{DE}}$ 0.0223

TABLE 2

Data Sheet: Isopropyl Ether, S368
(Lot 105 Charcoal/100 mg; Samples Stored 5 Days)

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.16	2.904	0.919	6.33	5.93	0.937	12.58	11.78	0.936
3.16	2.930	0.927	6.33	6.13	0.968	12.58	11.69	0.929
3.16	5.63*	1.782*	6.33	5.97	0.943	12.58	11.73	0.932
3.16	2.911	0.921	6.33	6.09	0.962	12.58	11.73	0.932
3.16	2.885	0.913	6.33	5.98	0.945	12.58	11.71	0.931
3.16	2.902	0.918	6.33	5.95	0.940	12.58	11.71	0.931
n =		5			6			6
mean		0.920			0.949			0.932
std dev		0.00508			0.0127			0.00232
CV_1		0.00552			0.0134			0.00249

$\overline{CV}_1$ 0.00866

$\overline{CV}_{A+\overline{DE}}$ 0.00936

*These values excluded from statistical analysis

TABLE 3

Data Sheet: Isopropyl Ether, S368
(Lot 105 Charcoal/100 mg; Samples Stored 5 Days)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mgΔ	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.698	2.870	2.872	999	992	
	2.771	2.948	2.833	1041	992	
	2.915	3.101	2.988	1038	992	
	2.972	3.162	3.074	1029	992	
	3.051	3.246	3.096	1048	992	
	2.754	2.930	3.031	967	992	
			n = 6			
			mean	1020		1.028
			std dev	31.2		
			CV_2	0.0306		
1S	5.98	6.36	2.910	2186	2069	
	5.84	6.21	2.872	2162	2069	
	5.88	6.25	2.872	2176	2069	
	5.69	6.05	2.794	2165	2069	
	5.71	6.07	2.833	2143	2069	
	5.47	5.82	2.833	2054	2069	
			n = 6			
			mean	2148		1.038
			std dev	48.1		
			CV_2	0.0224		
2S	11.27	11.99	2.794	4290	4260	
	11.27	11.99	2.833	4230	4260	
	11.56	12.30	2.872	4280	4260	
	9.97*	10.61*	3.031	3500*	4260	
	10.73	11.41	2.794	4080	4260	
	11.46	12.19	2.833	4300	4260	
			n = 5			
			mean	4240		0.995
			std dev	91.3		
			CV_2	0.0215		
			$\overline{CV}_2$	0.0254		

ΔCorrected for DE factor
*These values excluded from statistical analysis based on Grubb's test.

of the samples at the 2S test level were analyzed and no detectable amount of isopropyl ether was found. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 22 mg of isopropyl ether when a test atmosphere containing 4260 mg/cu m of isopropyl ether in air was sampled at 0.198 liter per minute for 26 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1; calculations were done using the data in Tables 2 and 3.

$\overline{CV}_1 = 0.0087$ $\overline{CV}_2 = 0.0254$ $\overline{CV}_T = 0.0562$

The average recovery of the generated samples over all levels for the sample stored for 5 days was 102.0%.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Backup Data Report

Substance:	Magnesium Oxide Fume, No. S369
OSHA Standard:	15 mg/cu m
Chemical Used for Validation:	Magnesium acetate Matheson, Coleman and Bell

Procedure

The procedure followed for validation of the method for collecting and measuring magnesium oxide fume in air is described in NIOSH Method S369, which was adapted from P&CAM 173. The reliability of the analytical method was tested at concentrations approximately equal to that present in a 150-liter sample at 0.5, 1, and 2 times the OSHA standard. Appropriate amounts of 325 mesh magnesium oxide were added to 37-mm/0.8-micron Type AA MCEF filters. The filters were digested in concentrated nitric acid to solubilize the magnesium oxide and destroy the organic matrix.

The ashed analyte was dissolved in 10 ml of concentrated nitric acid and diluted to 100 ml with deionized water prior to AA analysis. Analyses were done on a Varian Techtron AA6 atomic absorption spectrophotometer. The absorbance, measured at 202.5 nm, was used as a measure of the magnesium concentration in the sample when compared to samples of known concentrations. This procedure was also used for the analysis of 18 generated samples, six each at 0.5X, 1X, and 2X the OSHA standard. Details of the analytical procedure may be found in Section 8.4 of NIOSH Method No. S369.

Modifications

No major modifications to P&CAM 173 were made.

Generation

Samples of magnesium oxide particulate were generated by thermal decomposition and oxidation of a magnesium acetate aerosol. An Environmental Research Corporation fluid atomization aerosol generator was used to generate magnesium acetate aerosol from a 10% weight/volume solution of $Mg(C_2H_3O_2)_2$ in water. Oxygen was used to generate the aerosol to assure complete oxidation of the acetate upon its decomposition. The aerosol stream (flow rate of 10.64 liters/minute) did not undergo classification through an impaction device, because the 2X level for magnesium oxide was sufficiently high that it necessitated the use of the entire aerosol output.

The magnesium acetate aerosol/O_2 output from the generator entered a 24-in x 1-in I.D. quartz tube. The initial 12-in was heated by a tube furnace to approximately 1100°C. The final 12-in was wrapped in heating tape and heated to the limiting temperature of the tape at 110 volts. The energy supplied by the heating tape was necessary to maintain the extreme temperature obtained in the tube furnace. The temperature of the gases (at a flow rate of 10.64 liters/minute) leaving the quartz tube was approximately 450°C, 130°C above the decomposition temperature of magnesium acetate.

The average residence time of a particle in the furnace, at temperatures of at least 450°C, is 1.7 seconds. This is ample time to allow decomposition of the magnesium acetate and its complete oxidation to magnesium oxide. This was verified by several experiments. Samples of the generated material were submitted for index of refraction and X-ray diffraction analyses. Both procedures showed the presence of magnesium oxide. Optical and electron microscopy showed the particles to be entirely in the submicron size range.

The concentration in the generator was monitored using the Thermo-Systems Model 3200 Particle Mass Monitor. The output of the fluid atomization aerosol generator was held constant at 10.64 liters/minute while the dilution air flow rate was changed to achieve the desired concentration levels. No dilution air was used for the generation of the 2X level; for the 1X level a flow rate of 11 liters/minute was used and for the 0.5X level 32 liters/minute of dilution air. Samples were collected for 100 minutes at an average flow rate of 1.485 liter/minute.

Collection Efficiency

Collection efficiency at a concentration of 28.62 mg/cu m was determined by measuring the amount of particulate collected on each of the two filters in series mounted in direct contact with each other. The collection efficiency of the filter was found to be 1.00 at a detection limit of 0.333 mg/cu m. Thus, no correction for collection efficiency is needed in this method.

mg/cu m front filter	mg/cu m backup filter	Collection Efficiency
29.05	N.D.*	1.00
28.34	"	1.00
29.53	"	1.00
28.02	"	1.00
27.90	"	1.00
28.85	"	1.00

* Not detected at a detection limit of 0.333 mg/cu m.

Precision and Accuracy

The statistical procedures used are described in Reference No. 1.

$\overline{CV}_1 = 0.035$ $\overline{CV}_2 = 0.033$ $\overline{CV}_T = 0.062$

Data Sheet: Magnesium Oxide Fume S369

Analysis

Level	0.5S			1S			2S	
mg taken	mg found	DE	mg taken	mg found	DE	mg taken	mg found	DE
1.187	1.137	0.958	2.435	2.500	1.027	4.66	4.69	1.006
1.130	1.150	1.018	2.310	2.443	1.058	4.67	4.73	1.013
1.110	1.100	0.991	2.113	2.133	1.009	4.68	4.49	0.959
1.138	1.150	1.011	2.340	2.340	1.000	4.57	4.44	0.972
1.130	1.100	0.973	2.495	2.340	0.938	4.56	4.48	0.982
1.145	1.225	1.070	2.440	2.483	1.018	4.51	4.48	0.993
n =		6			6			6
mean		1.003			1.008			0.988
std dev		0.040			0.040			0.021
CV_1		0.040			0.040			0.021

$\overline{CV}_1$ 0.035

$\overline{CV}_{A+\overline{DE}}$ 0.038

No Analytical Method Recovery (A.M.R.) correction is necessary, since the A.M.R. at each level is essentially 1.00.

Data Sheet: Magnesium Oxide Fume S369

Sampling and Analysis

Test Level		Found		
		mg	Liters	mg/cu m*
0.5S		1.120	148.0	7.57
		1.238	153.5	8.07
		1.007	140.2	7.18
		1.084	149.9	7.23
		1.161	151.6	7.66
		1.058	148.0	7.15
			n = 6	
			mean	7.48
			std dev	0.36
			CV_2	0.048
1S		2.165	148.0	14.63
		2.345	153.5	15.28
		2.087	140.2	14.89
		2.190	149.9	14.61
		2.242	151.6	14.79
		2.138	148.0	14.45
			n = 6	
			mean	14.78
			std dev	0.29
			CV_2	0.020
2S		4.30	148.0	29.05
		4.35	153.5	28.34
		4.14	140.2	29.53
		4.20	149.9	28.02
		4.23	151.6	27.90
		4.27	148.0	28.85
			n = 6	
			mean	28.62
			std dev	0.64
$\overline{CV}_2$	0.033		CV_2	0.022

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

2. Backup Data Report, Methyl Cellosolve, No. S79, prepared under NIOSH Contract CDC-99-74-45.

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Backup Data Report

Substance: Methyl Bromide, No. S372

OSHA Standard: 80 mg/cu m (Ceiling)

Chemical used for validation: Methyl Bromide, Linde Specialty Gases, 99.5%

Procedure

The general procedure used is described in NIOSH Method No. S372 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of methyl bromide gas or a solution of methyl bromide in carbon disulfide represented in an 11-liter air sample. The charcoal used was Lot 104 petroleum-based charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in 5-ml tubes with Teflon-lined screw caps. Alternatively, the 5-ml vials with Teflon-lined screw caps distributed by SKC, Inc., were also used. Sample vials or tubes were capped tightly immediately after the addition of carbon disulfide to minimize loss of methyl bromide during the desorption process. After the 30-minute desorption period, a portion of the carbon disulfide extracts was transferred to the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using decane as internal standard. The appropriate DE correction factor used was determined from the "hand-drawn" DE curve. Details of the analysis procedure may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 has been modified as follows: The sampling tube series recommended consists of two separate tubes--a front adsorbing tube containing 400 mg of charcoal (prepared from a regular commercially available large tube by removing the backup section) and connected in series with a short piece of tubing to a second tube containing 200 mg of charcoal (similarly prepared from a regular large tube by removing the front section). The charcoal from each front and backup tube is desorbed with 2 ml of carbon disulfide.

Discussion

The initial experiments with methyl bromide were done on Lot 105 activated coconut charcoal containing the 100-mg front and 50-mg backup sections. Breakthrough studies on these charcoal tubes indicated a capacity of up to 2.5 liters of sample when sampling a test atmosphere containing 158 mg/cu m at 0.2 liter per minute. Correspondingly 18 analytical samples were prepared by adding the equivalents of 0.028, 0.056 and 0.112 mg of methyl bromide to 100 mg of Lot 105 charcoal contained in the automatic sample injector vials, using a solution of

methyl bromide in carbon disulfide. This solution was prepared by bubbling methyl bromide gas in carbon disulfide and assaying the resulting solution by comparison with methyl bromide gas standards. As shown in Table 1, the desorption efficiency is low with an average value of 0.45.

Subsequently the large Lot 104 charcoal tubes, containing the 400-mg front and 200-mg backup sections were tried. Breakthrough experiments conducted on six tubes containing only the 400-mg front section at 2X the OSHA standard and a sampling rate of 0.2 liter per minute indicated a feasible sample size of 11 liters.

The analytical procedure was modified to accommodate the 400 mg of charcoal used for these experiments. The 5-ml test tubes and the 5-ml SKC vials with Teflon-lined screw caps were used to hold the 400 mg of charcoal and the 2 ml of carbon disulfide required for the desorption. Early experiments with methyl bromide indicated that it was necessary to cap the vials tightly immediately after the addition of carbon disulfide; otherwise, lower recoveries and a greater scatter of data are observed.

Tests were also conducted to verify whether the samples can be transferred from the desorption tubes to the automatic sample injector vials without significant sample losses. Thus, a few experiments were done such that 5-µl aliquots of the desorbed samples were withdrawn directly from the vials or tubes used for desorption and then injected manually into the gas chromatograph. Portions of the remaining solution in the desorption tubes were then carefully transferred to the 2-ml automatic sample injector vials and analyzed using the automatic sample injector. There were no significant differences observed between these two approaches as shown in the comparative data summarized below, and thus the automatic sample injector was used for all subsequent experiments.

	---------- mg Methyl Bromide found by ----------	
Sample Code	Manual Injection	Automatic Sample Injection
1	0.25	0.25
2	0.26	0.26
3	0.24	0.22
4	0.85	0.96
5	0.93	0.98
6	1.04	1.06

For the preparation of spiked samples, experiments were done to compare the desorption efficiency obtained when methyl bromide gas was added directly to the charcoal relative to the use of methyl bromide solution

Table 1

DE on Lot 105/100-mg charcoal; Sample Size = 0.75 liter

Test Level: mg added:	0.5S (0.028 mg)		1S (0.056 mg)		2S (0.112 mg)	
	mg Found	DE	mg Found	DE	mg Found	DE
	0.0127	0.454	0.0274	0.489	0.0438	0.391
	0.0136	0.486	0.0274	0.489	*	*
	0.0146	0.521	0.0252	0.450	0.0444	0.396
	0.0127	0.454	0.0262	0.468	0.0513	0.458
	0.0125	0.446	0.0241	0.430	0.0484	0.432
	0.0142	0.507	0.0235	0.420	0.0501	0.447
	mean	0.478		0.458		0.425
	std dev	0.031		0.029		0.030
	CV	0.066		0.064		0.071

$\overline{CV} = 0.067$

* Sample lost

in carbon disulfide. There was no significant difference in desorption efficiency results obtained by these two methods, i.e., the D.E. values obtained were 0.81 and 0.83 respectively for spikes using the solution method (0.80 mg of methyl bromide added) and for the gas spikes (0.85 mg of methyl bromide added).

A survey test was also conducted to determine whether the methyl bromide collected in the front section tends to migrate to the backup section on storage. The data summarized in Table 2 for a sample size of 11 liters show significant amounts of methyl bromide in the backup section for samples stored for seven days prior to analysis. Note that the backup sections of samples analyzed immediately after collection show only trace amounts of methyl bromide. Thus, the recommended sampling procedure specifies the use of two separate tubes containing the 400-mg front and the 200-mg backup sections.

Generation

Test atmosphere samples were generated by delivering methyl bromide gas from a cylinder via an orifice and needle valve to a dry air stream flowing at a rate of 0.100 cu m/min. The generator concentration was determined based on a calibration curve prepared by dosing M^3 with known amounts of methyl bromide gas and measuring the hydrocarbon response using a total hydrocarbon analyzer. The details of this calibration procedure are described in the Propane, S87, Backup Data Report. Using this method, the generator concentration was determined to be 34.9, 75.0, and 150.4 mg/cu m respectively at the test levels equivalent to the 0.5, 1 and 2X OSHA standard. All six samples at the three test levels were collected simultaneously at 1.1 liters per minute for 10 minutes (11 liters). These samples were stored for seven days before desorption and analysis. Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 2.9 mg of methyl bromide when a test atmosphere containing 161 mg/cu m of methyl bromide in air was sampled at 0.19 liter per minute for 94 minutes; at that time the concentration of analyte in the effluent was 5% of that in the influent.

In addition, the backup sections of the 11-liter samples collected at 1.1 liters per minute at 2X the OSHA standard level were also analyzed. Only trace amounts of methyl bromide were found in any of the six backup tubes analyzed; the minimum detectable level is 0.010 mg/2 ml.

Precision and Accuracy

As described in Reference 1, Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for methyl bromide.

Table 2

Methyl Bromide: Migration Effects on Storage

Lot 104/400-mg Tubes

(Sample Stored for Seven Days with Backup Section)

Test Level:	mg Found			
	Front	Backup	Total	% Found in Backup
0.5S	0.183	0.036	0.219	16.4
	0.197	0.021	0.218	9.6
	0.182	0.016	0.198	8.1
	0.207	0.021	0.228	9.2
	0.210	0.025	0.235	10.6
	0.214	0.013	0.227	5.7
			Average	9.9
1S	0.387	0.046	0.433	10.6
	0.495	0.086	0.581	14.8
	0.536	0.076	0.612	12.4
	0.484	0.099	0.583	17.0
	0.496	0.079	0.575	13.7
	0.477	0.076	0.553	13.7
			Average	13.7
2S	1.158	0.305	1.463	20.9
	1.056	0.252	1.308	19.3
	1.083	0.283	1.366	20.7
	1.081	0.294	1.375	21.4
	1.173	0.263	1.436	18.3
	1.127	0.277	1.404	19.7
			Average	20.1

The sampling and analysis data gave a chi squared value of 15.62 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for methyl bromide, however, still show reasonably good precision and therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 2.

$$\overline{CV}_1 = 0.0530 \qquad \overline{CV}_2 = 0.0882 \qquad \overline{CV}_T = 0.103$$

The average recovery of the generated samples over all levels was 96.5%. It should be noted that the recovery values shown in the last table were based on DE values for analytical spike samples stored for only one day while the collected samples were stored for seven days. This difference in sample age may account for the observed lower recovery trend for the 0.5S level. DE studies with a few selected compounds indicate that the decrease in DE with time is most pronounced at the 0.5S level.

References

1. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Data Sheet: Methyl Bromide, S372

(Lot 104/400-mg; Stored 1 day only)

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
0.403	0.293	0.727	0.806	0.708	0.878	1.612	1.267	0.786
0.403	0.315	0.782	0.806	0.689	0.855	1.612	1.293	0.802
0.403	0.280	0.695	0.806	0.614	0.762	1.612	1.374	0.852
0.403	0.282	0.700	0.806	0.590	0.732	1.612	1.301	0.807
0.403	0.297	0.737	0.806	0.682	0.846	1.612	1.378	0.855
0.403	0.278	0.690	0.806	0.655	0.813	1.612	1.340	0.831
n =		6			6			6
mean		0.722			0.814			0.822
std dev		0.0349			0.0570			0.0283
CV_1		0.0483			0.0700			0.0344

$\overline{CV_1}$ 0.0530

$\overline{CV_A} + \overline{DE}$ 0.0572

Data Sheet: Methyl Bromide, S372

(Lot 104/400-mg Front and Separate Backup Sections, Stored 7 Days)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.240	0.338	11.12	30.4	34.9	
	0.227	0.322	10.94	29.4	34.9	
	0.244	0.344	10.94	31.4	34.9	
	0.242	0.341	11.10	30.7	34.9	
	0.238	0.335	11.03	30.4	34.9	
	0.231	0.328	10.98	29.9	34.9	
			n = 6			
			mean	30.4		87.1
			std dev	0.683		
			CV_2	0.0225		
1S	0.656	0.815	11.05	73.8	75.0	
	0.613	0.766	11.11	68.9	75.0	
	0.686	0.847	11.25	75.3	75.0	
	0.605	0.756	11.14	67.9	75.0	
	0.642	0.798	11.04	72.3	75.0	
	0.634	0.788	11.05	71.3	75.0	
			n = 6			
			mean	71.6		95.5
			std dev	2.83		
			CV_2	0.0395		
2S	1.074	1.302	10.80	120.6	150.4	
	1.531	1.856	10.87	170.7	150.4	
	1.288	1.571	10.76	146.0	150.4	
	1.538	1.864	11.07	168.4	150.4	
	1.601	1.941	11.06	175.5	150.4	
	1.672	2.014	10.94	184.1	150.4	
			n = 6			
			mean	160.9		107.0
			std dev	23.45		
			CV_2	0.1458		
			$\overline{CV}_2$	0.0882		

Backup Data Report

Substance: Molybdenum, Insoluble Compounds, No. S376

OSHA Standard: 15 mg/cu m

Chemical Used for Validation: Sodium Molybdate, Fisher Scientific Co., certified

Procedure

The general procedure used is described in NIOSH Method No. S376 which is a modification of P&CAM 173 for filter collection and analysis of metal particulates by atomic absorption spectrophotometry. The reliability of the analytical method was tested at sample concentrations equal to that present in a 90-liter sample at 0.5, 1 and 2 times the OSHA standard. The appropriate aliquot of a solution of sodium molybdate in water was added to eighteen 37 mm Type AA Millipore filters; the aliquots added contained Mo equivalent to the 3 test levels of interest. Another set of 18 spiked samples was also prepared by adding weighed amounts of molybdenum oxide, MoO_3, to the appropriate 37 mm filters contained in Phillips beakers; again the weighed amount of MoO_3 added contained Mo equivalent to the 3 test levels of interest. (Refer to discussion section.)

The analyte was recovered from the filter by digestion with nitric and perchloric acid to destroy the organic filter matrix. A few drops of concentrated sulfuric acid was added to dissolve the white precipitate formed. The solutions were analyzed with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The absorbance, measured at 313.3 nm, was used as a measure of molybdenum concentration in the sample. Appropriate standard solutions were analyzed alternately with samples to minimize observed variations in flame responses during any given day. Similarly, the 18 generated samples (6 at each of the 0.5, 1 and 2X OSHA standard levels) were analyzed accordingly. Details of the digestion and analytical procedures may be found in Section 8.3 of NIOSH Method No. S376.

Modification

Several modifications of P&CAM 173 were adapted in order to meet the specific requirements of the molybdenum assay. These modifications were:

a. digestion with nitric and perchloric acid (for acid soluble compounds of Mo)
b. addition of concentrated sulfuric acid
c. addition of aluminum
d. analysis by alternating samples with calibration standards

The nitric acid/perchloric acid digestion procedure adapted for acid soluble molybdenum compounds was found to give good recoveries. The average values found were 100% and 103.5% respectively for analytical samples containing sodium molybdate and molybdenum oxide. A different digestion procedure is recommended for base soluble molybdenum compounds.

A few drops of concentrated sulfuric acid were added to the digestion liquor after the final acid digestion step. This treatment is necessary because at these high concentrations of molybdenum (as sodium molybdate and molybdenum oxide), a white, hydrochloric acid-insoluble residue of unknown composition remains in the beaker after the digestion procedure. This residue is soluble in concentrated sulfuric acid and good recoveries were obtained only when sulfuric acid was added.

A fixed amount of aluminum was added in order to control the variable enhancement which occur due to acidity and variable amounts of aluminum contaminants. The addition of aluminum also improves accuracy as indicated by data presented in dicussion section.

The analysis procedure was also modified such that a calibration curve is not used, instead samples are analyzed alternately with standards. This procedure is necessary because it has been observed that there is a marked decrease in the slope of the calibration curve obtained at the beginning of the day as compared to subsequent calibration runs. These variations are believed to be due to carbon buildup at the burner head.

Discussion

The OSHA standard as specified is for molybdenum, insoluble compounds (i.e., water-insoluble). However, the experiments on the generation of the sample test atmosphere were carried out using a water soluble molybdenum compound (sodium molybdate) in order to simplify the sample generation process. Since all the water-insoluble molybdenum compounds would exist as a particulate, the generation and collection experiment conducted is a valid representation covering the general category of insoluble molybdenum compounds. The only other issue which must be addressed is the applicability of the analytical method, i.e., the filter digestion and sample dissolution procedure, for the quantitative recovery of water-insoluble molybdenum compounds.

The water-insoluble compounds of molybdenum listed in the Handbook of Chemistry and Physics can be classified under the following general categories:

a. Soluble in both acid and base, such as MoO_3, $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$.

b. Soluble in acid only such as MoC, Mo_2O_5, MoO_2.

c. Soluble in base only such as $MoBr_3$, $MoBr_2$.

d. Insoluble in acid or base such as Mo_2O_3.

There are relatively few molybdenum compounds which fall under the c & d category; in addition, the base soluble compound $MoBr_3$ is not available commercially and attempts to procure $MoBr_2$ failed. Thus, the experimental work on the analytical method was carried out using MoO_3 as the representative of the insoluble compounds of molybdenum.

The analytical method recovery experiments were conducted using 18 filter samples spiked with known amounts of an aqueous solution of sodium molybdate and 18 filters loaded with weighed amounts of MoO_3. In each case, the Mo added to the filters was equivalent to the amount present in a 90-liter sample at the 3 test levels of 0.5, 1 and 2X OSHA standard. All samples were treated by the nitric/perchloric acid digestion and sulfuric acid dissolution procedure for acid soluble molybdenum compounds described in Section 8.3 of NIOSH Method No. S376. The data for the sodium molybdate-spiked samples summarized in Table 1 show an average recovery of 100% with $\overline{CV}_1$ = 0.0165. The samples spiked with MoO_3 gave equally good recovery and precision, 103.5% with $\overline{CV}_1$ = 0.028, as shown in Table 2.

Since MoO_3 is not only acid soluble but also base soluble, a secondary analytical experiment was conducted using six samples spiked with weighed amounts of MoO_3. The samples were treated with 2N sodium hydroxide prior to the digestion of the filter with nitric acid. White sodium nitrate crystals appear during the final stages of the acid digestion process. The samples were treated with concentrated sulfuric acid, aluminum was added and the sample was taken up in distilled water and diluted to volume. The white, crystalline precipitate formed redissolves during the final dilution with water. The data for these six samples shown in Table 3 also gave good recovery and precision, 98.5% with CV_1 = 4.9%. It should be noted that the reference standards used for these analyses were prepared using the respective components used in the sample processing, i.e., sodium nitrate was added to reference standards for this set of samples.

Another information obtained during these studies relates to the fact that if aluminum is not added to the samples, poor recovery and precision were obtained. Analytical samples spiked with MoO_3 at levels equivalent to 0.5 and 1X OSHA standard for a 90 liter sample showed respective recoveries of 83% (CV_1 = 0.057) and 81% (CV_1 = 0.070) as shown in Table 4. All data are based on the analysis of samples without added aluminum and compared with calibration standards also without added aluminum.

Table 1

Data Sheet: Molybdenum, Insoluble Compounds, S376

Analysis*

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
675	650	0.963	1350	1310	0.970	2700	2850	1.056
675	650	0.963	1350	1310	0.970	2700	2900	1.074
675	635	0.941	1350	1300	0.963	2700	2900	1.074
675	650	0.963	1350	1375	1.019	2700	2925	1.083
675	635	0.941	1350	1350	1.000	2700	2825	1.046
675	650	0.963	1350	1350	1.000	2700	2875	1.065
n =		6			6			6
mean		0.956			0.987			1.066
std dev		0.0114			0.0224			0.0135
CV_1		0.0119			0.0227			0.0127

$\overline{CV}_1$ 0.0165

$\overline{CV}_{A+\overline{CE}}$ 0.0178

*These data are based on the analysis of samples spiked with known aliquots of an aqueous standard solution of sodium molybdate; all data are expressed as µg Mo.

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Table 2

Data Sheet: Molybdenum, Insoluble Compounds, No. S376

Analysis*

Level	0.5S			1S			2S		
	µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
	541	551	1.018	1156	1167	1.010	2953	3190	1.080
	708	724	1.023	1016	1056	1.039	3570	3690	1.034
	222	238	1.072	1081	1090	1.008	3590	3680	1.025
	403	428	1.062	1340	1408	1.051	3190	3110	0.975
	383	404	1.055	980	1019	1.040	2556	Sample	Lost
	269	290	1.078	1036	1030	0.994	3480	3610	1.037
n =		6			6			5	
mean		1.051			1.024			1.030	
std dev		0.0252			0.0226			0.0375	
CV_1		0.0240			0.0221			0.0364	

$\overline{CV}_1$ 0.0282

$\overline{\overline{CV}}_{A+\overline{DE}}$ 0.0305

*These data are based on the analysis of samples spiked with weighed amounts of MoO_3; all data are expressed as µg Mo.

Table 3

MoO_3 Analytical Samples Treated with NaOH

µg Mo Added	µg Mo Found	Recovery
1447	1454	1.005
1327	1336	1.007
1440	1454	1.010
1182	1218	1.030
1708	1630	0.954
2191	1975	0.901
	mean	0.985
	CV_1	0.049

Table 4

Molybdenum Recovery, No Al Added

µg Mo Added	µg Mo Found	Recovery	µg Mo Added	µg Mo Found	Recovery
527	412	0.782	1825	1602	0.878
597	500	0.838	1493	1109	0.743
659	525	0.797	1443	1113	0.771
714	655	0.917	1850	1633	0.883
732	606	0.828	1429	1179	0.825
958	781	0.815	1330	1051	0.790
n =		6			6
mean		0.830			0.815
std dev		0.0474			0.0573
CV_1		0.0572			0.0704

Generation

Test atmosphere samples at a concentration 2X the OSHA standard level were generated by atomization of an aqueous sodium molybdate solution containing 14.8 g/liter as molybdenum into a dry, solvent-free air stream flow. The equipment assembly used to generate the test aerosol is shown in Figure 1. A solution mist was generated with a DeVilbiss Model 35A ultrasonic nebulizer. Filtered air (2.75 lpm), which had been saturated by bubbling through two gas scrubbers containing distilled water, was passed through the nebulizer to pick up the mist and carry it to an aluminum chamber where it was mixed with dry air. The aerosol then entered the mainline of the dilution system described in the Octachloronaphthalene S97 Backup Data Report. The generation/dilution system was operated so that a 2X OSHA standard level was produced in the mainline, then twofold and fourfold dilutions were made to obtain 1 and 0.5 times the OSHA standard level. All 6 samples at the three test levels were collected simultaneously at 1.5 liters per minute for 60 minutes (90 liters). Since collection efficiency was found to be 100%, the concentration in the generator and the "found" concentration were considered to be equal. Details of the sample generation/dilution system and collection equipment may be found in the Octachloronaphthalene S97 Backup Data Report and Attachment.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for particulate soluble molybdenum compounds was determined by collecting two sets of six filter samples at air sample concentrations of 31 and 53 mg/cu m. The physical layout of the filter series (front and backup) used for each of the two sets of six samples collected was such that the two filters were mounted back to back in contact with each other and supported by the backup pad. The average collection efficiency found was 100% for both series (Table 5).

Precision and Accuracy

The statistical procedures used are described in Reference 1; the data used are summarized in Tables 2 and 6.

$$\overline{CV}_1 = 0.0282 \qquad \overline{CV}_2 = 0.0232 \qquad \overline{CV}_T = 0.056$$

The collection efficiency was found to be 100% and the analytical method recovery based on the analysis of 36 samples was 101.7%. Since there was no bias in the determination, the generator concentration and the "found" concentration were considered to be equal. Thus, CV_T is a measure of both accuracy and precision.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

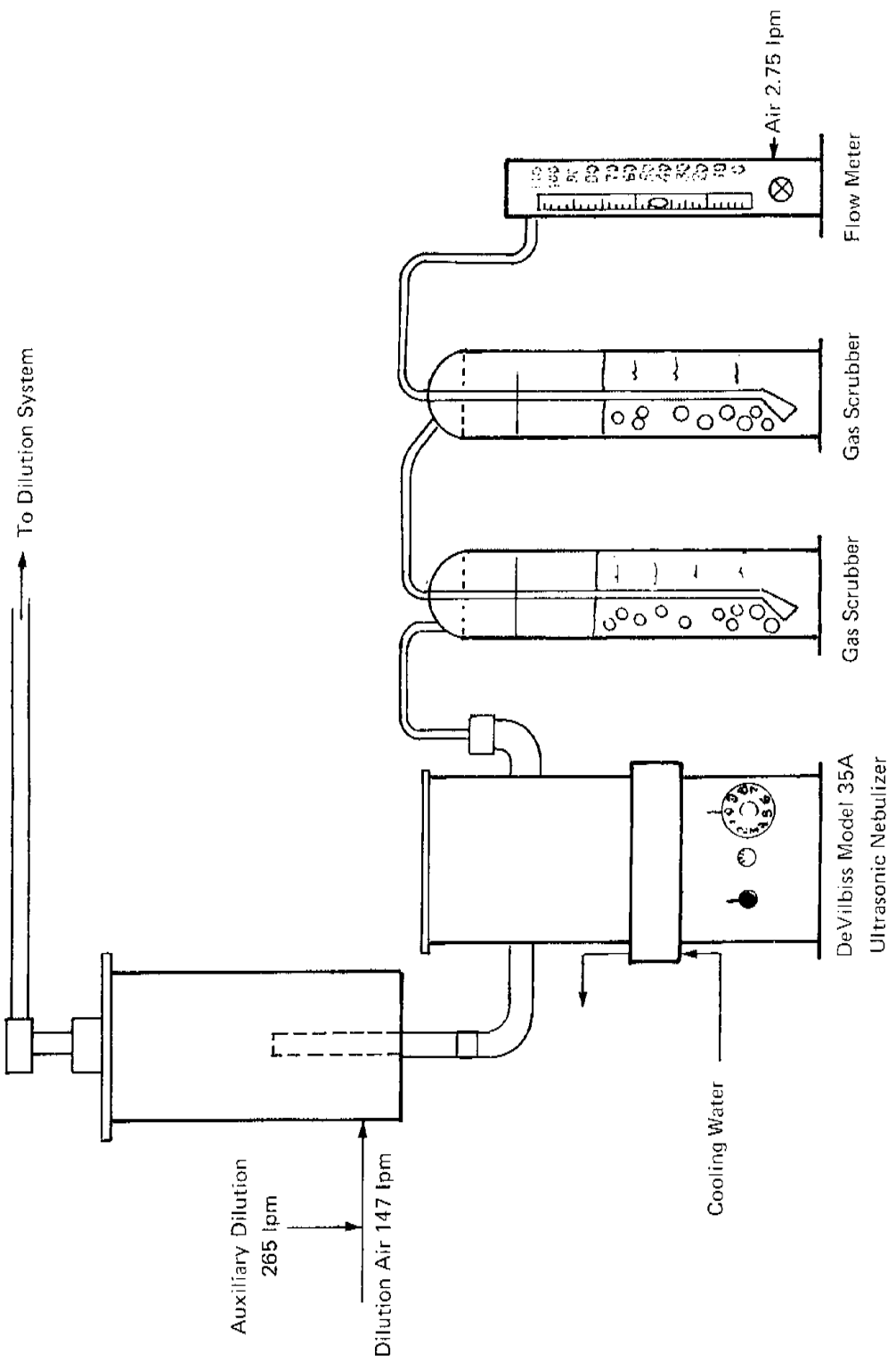

FIGURE 1 AEROSOL GENERATOR FOR MOLYBDENUM, INSOLUBLE COMPOUNDS

Table 5

Collection Efficiency: Molybdenum, Insoluble Compounds, S376

Test Level mg/cu m	µg Found			% Collected in Front
	Front	Backup	Total	
53	4400	ND	4400	100
	4950	ND	4950	100
	4625	ND	4625	100
	4950	ND	4950	100
	4600	ND	4600	100
	4950	ND	4950	100
		Average Collection Efficiency		100%
31	2810	ND	2810	100
	2640	ND	2640	100
	2740	ND	2740	100
	2800	ND	2800	100
	2800	ND	2800	100
	2810	ND	2810	100
		Average Collection Efficiency		100%

ND - No detectable molybdenum; the limit of detection was 0.3 µg/ml x 50 ml = 15 µg/50 ml

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Table 6

Data Sheet: Molybdenum, Insoluble Compounds, S376

Sampling and Analysis**

Test Level	Found		
	µg	Liters	µg/ℓ or mg/cu m
0.5S	575	90.3	6.37
	565	90.0	6.28
	575	89.7	6.41
	540	90.2	5.99
	*	89.9	*
	575	90.7	6.34
		n = 5	
		mean	6.28
		std dev	0.1678
		CV_2	0.0267
1S	1265	90.4	13.99
	1240	90.6	13.69
	1225	90.1	13.60
	1220	90.8	13.44
	1235	91.2	13.54
	1285	90.7	14.17
		n = 6	
		mean	13.74
		std dev	0.2827
		CV_2	0.0206
2S	2810	90.4	31.1
	2800	90.3	31.0
	2800	90.4	31.0
	2740	90.3	30.3
	2640	90.1	29.3
	2810	91.1	30.8
		n = 6	
		mean	30.6
		std dev	0.691
		CV_2	0.0226
		$\overline{CV}_2$	0.0232

*Sample lost

**These data are based on generated smaples using sodium molybdate as model compound.

Backup Data Report

Substance: Octane

OSHA Standard: 2350 mg/cu m

Chemical used for
validation: Octane, Aldrich 99 + % Gold Label

Procedure

The general procedure used is described in NIOSH Method No. S378 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of octane represented in a 4 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 454 mg/min of octane via a syringe injector to a dry air stream flowing at a rate of 0.1031 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 30 mg of octane when a test atmosphere containing 4612 mg/cu m of octane in air was sampled at 0.19 liters per minute for 34 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data are based on a prior experiment.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for octane as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 10.9, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for octane show excellent precision. Therefore, pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0089 \qquad \overline{CV}_2 = 0.0321 \qquad \overline{CV}_T = 0.0595$$

The average recovery of the generated samples over all levels was

$$98.2 \pm 7.8\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Octane S378

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.75	4.47	0.941	9.78	9.32	0.953	18.86	18.18	0.964
4.75	4.39	0.924	9.78	9.07	0.927	18.86	18.11	0.960
4.75	4.40	0.926	9.78	9.23	0.944	18.86	18.21	0.966
4.75	4.41	0.928	9.78	9.18	0.939	18.86	18.45	0.978
4.75	4.42	0.931	9.78	9.25	0.946	18.86	18.23	0.967
4.75	4.38	0.922	9.78	9.22	0.943	18.86	17.90	0.949
n =		6			6			6
mean		0.929			0.942			0.964
std dev		0.00680			0.00867			0.00949
CV_1		0.00732			0.00921			0.00984

$\overline{CV_1}$ 0.00885

$\overline{CV}_{A+\overline{DE}}$ 0.00956

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Data Sheet: Octane S378
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.09	4.40	4.01	1097	1049	
	4.02	4.33	4.01	1080	1049	
	3.82	4.12	4.01	1027	1049	
	3.96	4.27	4.01	1065	1049	
	3.77	4.07	4.01	1015	1049	
	3.18*	3.44*	4.01	858*	1049	
			n = 5			
			mean	1057		100.8
			std dev	34.8		
			CV_2	0.0329		
1S	7.78	8.28	4.01	2065	2170	
	7.73	8.22	3.97	2070	2170	
	7.69	8.18	3.94	2075	2170	
	7.89	8.39	4.08	2055	2170	
	7.77	8.27	4.03	2050	2170	
	7.63	8.12	3.99	2035	2170	
			n = 6			
			mean	2058		94.8
			std dev	14.7		
			CV_2	0.00715		
2S	16.40	17.14	4.13	4150	4400	
	16.66	17.39	4.03	4320	4400	
	16.32	17.05	4.03	4230	4400	
	17.16	17.88	4.01	4460	4400	
	18.82	19.56	4.17	4690	4400	
	16.57	17.30	4.03	4290	4400	
			n = 6			
			mean	4360		98.9
			std dev	193.0		
			CV_2	0.0443		
			$\overline{CV}_2$	0.0321		

*These values excluded from statistical analysis

Backup Data Report

Substance: Pentane

OSHA Standard: 2950 mg/cu m

Chemical used for validation: Pentane, MC/B Chromatoquality

Procedure

The general procedure used is described in NIOSH Method No. S379 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of pentane represented in a 2-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report. For pentane, the back-up section of the charcoal tubes was also desorbed with 1.0 ml of carbon disulfide and analyzed in the usual manner. No evidence of pentane was found in the back-up sections of all the samples collected.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 603.1 mg/min of pentane via a syringe injector to a dry air stream flowing at a rate of 0.0975 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.067 liters per minute for 30 minutes (2 liters). The data reported are from the second set of 18 samples collected. The data for the first set of 18 samples gave a $\overline{CV}_2$ of 0.040, but a low average recovery - 86.8%. Note that for the second set of samples, the generator concentration was determined not only on the basis of the syringe delivery rate and air flow as noted above, but also by measuring the main line (2S) hydrocarbon concentration with a Beckman Model 402 Hydrocarbon Analyzer properly calibrated using reference gas standards. The pentane concentration by the former method is 6190 mg/cu m and agrees well with the total hydrocarbon data - 6170 mg/cu m.

Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

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Breakthrough

The first section of the charcoal tube was found to hold 18 mg of pentane when a test atmosphere containing 5640 mg/cu m of pentane in air was sampled at 0.19 liters per minute for 16.5 minutes; Breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for pentane as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 15.65 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for pentane show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0141 \qquad \overline{CV}_2 = 0.0220 \qquad \overline{CV}_T = 0.0549$$

The average recovery of the generated samples over all levels was

$$91.7 \pm 8.0\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Pentane S379

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.983	2.898	0.972	5.97	5.60	0.938	11.81	11.70	0.991
2.983	2.897	0.971	5.97	5.76	0.965	11.81	11.45	0.970
2.983	2.893	0.970	5.97	5.74	0.961	11.81	11.13	0.942
2.983	2.928	0.982	5.97	5.67	0.950	11.81	11.37	0.963
2.983	2.930	0.982	5.97	5.62	0.941	11.81	11.35	0.961
2.983	2.923	0.980	5.97	5.85	0.980	11.81	11.30	0.957
n =	6			6			6	
mean	0.976			0.956			0.964	
std dev	0.00574			0.0159			0.0162	
CV_1	0.00588			0.0167			0.0168	

$\overline{CV}_1$ 0.0141

$\overline{CV}_{A+\overline{DE}}$ 0.0152

Data Sheet: Pentane S379
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.633	2.728	2.00	1364	1476	
	2.655	2.751	1.97	1396	1476	
	2.852	2.955	2.08	1421	1476	
	2.775	2.876	2.14	1344	1476	
	2.877	2.981	2.15	1387	1476	
	2.637	2.733	2.11	1295	1476	
			n = 6			
			mean	1369		92.8
			std dev	44.4		
			CV_2	0.0325		
1S	5.39	5.59	2.03	2754	3040	
	5.39	5.59	2.00	2795	3040	
	5.09	5.28	2.00	2640	3040	
	5.13	5.32	1.94	2742	3040	
	5.28	5.47	1.97	2777	3040	
	5.24	5.43	1.97	2756	3040	
			n = 6			
			mean	2744		90.3
			std dev	54.3		
			CV_2	0.0198		
2S	10.67	11.06	1.94	5700	6190	
	10.78	11.17	1.97	5670	6190	
	10.97	11.37	2.00	5690	6190	
	11.65	12.07	2.11	5720	6190	
	10.66	11.05	1.94	5700	6190	
	10.85	11.24	1.97	5710	6190	
			n = 6			
			mean	5700		92.1
			std dev	17.22		
			CV_2	0.00302		
			$\overline{CV}_2$	0.0220		

Backup Data Report

Substance: Petroleum Distillate

OSHA Standard: 2000 mg/cu m

Chemical used for validation: VM&P Naphtha, Amsco Special Naphtholite 66/3 9300, Product Code 1101 (Boiling range: 120-147°C; density: 0.743 g/ml)

Procedure

The general procedure used is described in NIOSH Method No. S380 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of petroleum distillate represented in a 4-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using decane as internal standard. Petroleum distillate is a mixture of hydrocarbons and all data are based on integrating the total area of relevant peaks. Desorption efficiencies were determined by plotting the DE values obtained for the 0.5X,1X and 2X the OSHA standard and hand-drawing the best-fit curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 was used but the calibration technique was modified to include total measurement of all analyte-related peaks.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 394.9 mg/min of petroleum distillate via a syringe injector to a dry air stream flowing at a rate of 0.1005 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 24.6 mg of petroleum distillate when a test atmosphere containing 3930 mg/cu m of petroleum distillate in air was sampled at 0.19 liters per minute for 33 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for petroleum distillate as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 16.11 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for petroleum distillate show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0084 \qquad \overline{CV}_2 = 0.0132 \quad \overline{CV}_T = 0.0518$$

The average recovery of the generated samples over all levels was

$$95.7 \pm 7.4\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Petroleum Distillate S380

Analysis

Level	0.5S		1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.01	3.95	0.985	8.17	7.73	0.946	16.35	15.61	0.955
4.01	3.85	0.960	8.17	7.88	0.965	16.35	15.48	0.947
4.01	3.94	0.983	8.17	7.86	0.962	16.35	15.58	0.953
4.01	3.85	0.960	8.17	7.86	0.962	16.35	15.49	0.947
4.01	3.92	0.978	8.17	7.83	0.958	16.35	15.44	0.944
4.01	3.92	0.978	8.17	7.77	0.951	16.35	15.54	0.950
n =		6			6			6
mean		0.974			0.957			0.949
std dev		0.0112			0.00737			0.00413
CV_1		0.0115			0.00770			0.00435

$\overline{CV}_1$ 0.00838

$\overline{CV}_{A+\overline{DE}}$ 0.00905

Data Sheet: Petroleum Distillate S380
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.51	3.66	4.10	893	937	
	3.37	3.51	4.10	856	937	
	3.42	3.56	4.10	868	937	
	3.54	3.69	4.10	900	937	
	3.55	3.70	4.10	902	937	
	3.49	3.64	4.10	888	937	
			n = 6			
			mean	885		94.5
			std dev	18.52		
			CV_2	0.0209		
1S	7.18	7.48	4.10	1824	1932	
	7.21	7.51	4.06	1850	1932	
	7.15	7.45	4.02	1853	1932	
	7.47	7.78	4.17	1866	1932	
	7.36	7.67	4.11	1866	1932	
	7.20	7.50	4.08	1838	1932	
			n = 6			
			mean	1850		95.8
			std dev	16.37		
			CV_2	0.00885		
2S	15.41	16.05	4.22	3800	3930	
	15.02	15.65	4.11	3810	3930	
	15.03	15.66	4.11	3810	3930	
	14.93	15.55	4.10	3790	3930	
	15.60	16.25	4.26	3810	3930	
	14.99	15.61	4.11	3800	3930	
			n = 6			
			mean	3800		96.7
			std dev	8.16		
			CV_2	0.00215		
			$\overline{CV_2}$	0.0132		

Backup Data Report

Substance: Stoddard Solvent

OSHA Standard: 2950 mg/cu m

Chemical used for validation: Stoddard Solvent, Fisher Scientific Co. (Boiling range: 159-176°C; density: 0.774 g/ml)

Procedure

The general procedure used is described in NIOSH Method No. S382 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of Stoddard Solvent represented in a 3-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using undecane as internal standard. Stoddard Solvent is a mixture of hydrocarbons and all data are based on integrating the total area of relevant peaks. Desorption efficiencies were determined by plotting the DE values obtained for the 0.5X, 1X and 2X the OSHA standard and hand-drawing the best-fit curve. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

P&CAM 127 was used but the calibration technique was modified to include total measurement of all analyte-related peaks.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 599 mg/min of Stoddard Solvent via a syringe injector to a dry air stream flowing at a rate of 0.1008 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 13 minutes (3 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The breakthrough data below were obtained under different operating conditions.

The first section of the charcoal tube was found to hold 26.3 mg of Stoddard Solvent when a test atmosphere containing 6026 mg/cu m of Stoddard Solvent in air was sampled at 0.19 liters per minute for 23 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for Stoddard Solvent as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 11.9 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for Stoddard Solvent show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0108 \qquad \overline{CV}_2 = 0.0125 \qquad \overline{CV}_T = 0.0517$$

The average recovery of the generated samples over all levels was

$$96.8 \pm 7.4\%$$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Stoddard Solvent S382

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.49	4.41	0.982	9.28	8.83	0.952	18.57	17.37	0.935
4.49	4.38	0.976	9.28	9.06	0.976	18.57	17.39	0.936
4.49	4.33	0.964	9.28	8.81	0.949	18.57	17.43	0.939
4.49	4.31	0.960	9.28	8.85	0.954	18.57	17.26	0.929
4.49	4.29	0.955	9.28	8.76	0.944	18.57	17.36	0.935
4.49	4.42	0.984	9.28	8.73	0.941	18.57	17.52	0.943
n =		6			6			6
mean		0.970			0.953			0.936
std dev		0.0121			0.0124			0.00467
CV_1		0.0125			0.0130			0.00499

$\overline{CV}_1$ 0.0108

$\overline{CV}_{A+\overline{DE}}$ 0.0117

Data Sheet: Stoddard Solvent S382
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.98	4.18	2.95	1417	1417	
	3.92	4.11	2.95	1393	1417	
	3.96	4.16	2.95	1410	1417	
	3.89	4.08	2.95	1383	1417	
	3.86	4.05	2.95	1373	1417	
	3.94	4.13	2.95	1400	1417	
			n = 6			
			mean	1396		98.5
			std dev	16.49		
			CV_2	0.0118		
1S	7.97	8.36	2.95	2834	2921	
	7.90	8.29	2.99	2773	2921	
	7.46	7.83	2.90	2700	2921	
	1.86*	1.92*	3.00	640*	2921	
	7.97	8.36	2.96	2824	2921	
	7.77	8.15	2.93	2782	2921	
			n = 5			
			mean	2783		95.3
			std dev	53.1		
			CV_2	0.0191		
2S	16.57	17.39	3.04	5720	5940	
	16.23	17.03	2.96	5750	5940	
	16.23	17.03	2.96	5750	5940	
	16.13	16.93	2.95	5740	5940	
	16.76	17.59	3.07	5730	5940	
	16.25	17.05	2.96	5760	5940	
			n = 6			
			mean	5740		
			std dev	14.7		96.6
			CV_2	0.00256		
			$\overline{CV}_2$	0.0125		

*These values excluded from statistical analysis

Backup Data Report

Substance: Titanium Dioxide Dust, No. S385

OSHA Standard: 15 mg/cu m

Chemical Used for Validation: Titanium Dioxide, Fisher Scientific, certified

Procedure

The general procedure used is described in NIOSH Method No. S385 which is an adaptation of P&CAM 173 for the filter collection and analysis of metal particulates by atomic absorption spectroscopy. The reliability of the analytical method was tested at sample concentrations equivalent to that present in a 100-liter sample at 0.5, 1 and 2 times the OSHA standard. The analytical samples were prepared by adding weighed amounts of titanium dioxide into a series of eighteen 37-mm Type AA Millipore filters, each contained in a Phillips beaker. The titanium dioxide samples were weighed in Pt boats using an electronic balance. The sample and filters were digested with concentrated nitric acid and the analyte was solubilized by heating with a mixture of sulfuric acid and ammonium sulfate. Analyses were done with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The absorbance, measured at 364.3 nm, was used as a measure of the titanium concentration in the sample. Appropriate standard solutions were analyzed on the same day the samples were analyzed. A similar procedure was used for the analysis of the 18 generated samples, 6 at each of the 0.5, 1 and 2 times OSHA standard levels. Details of the analytical procedures may be found in Section 8.3 of NIOSH Method No. S385.

Modification

P&CAM 173 was modified by recommending the addition of sulfuric acid/ammonium sulfate to the sample solution as an aid to the complete dissolution of titanium dioxide.

Generation

The basic elements of the system used to generate the titanium dioxide atmospheres are shown in Figures 1 and 2. The system consists of a Wright Dust Feeder, an aerosol charge neutralizer, and an 80-liter stainless dust chamber.

Dust samples to be dispersed in the apparatus are compressed into a container which is attached to the Wright Dust Feeder. In operation, the container and the dust compact are slowly rotated and driven against a stationary scraper blade by an electrically-operated mechanism. The blade continuously removes dust from the compact surface at a uniform rate. Compressed air enters the container and entrains the dust particles. The dust holder advance rate may be varied

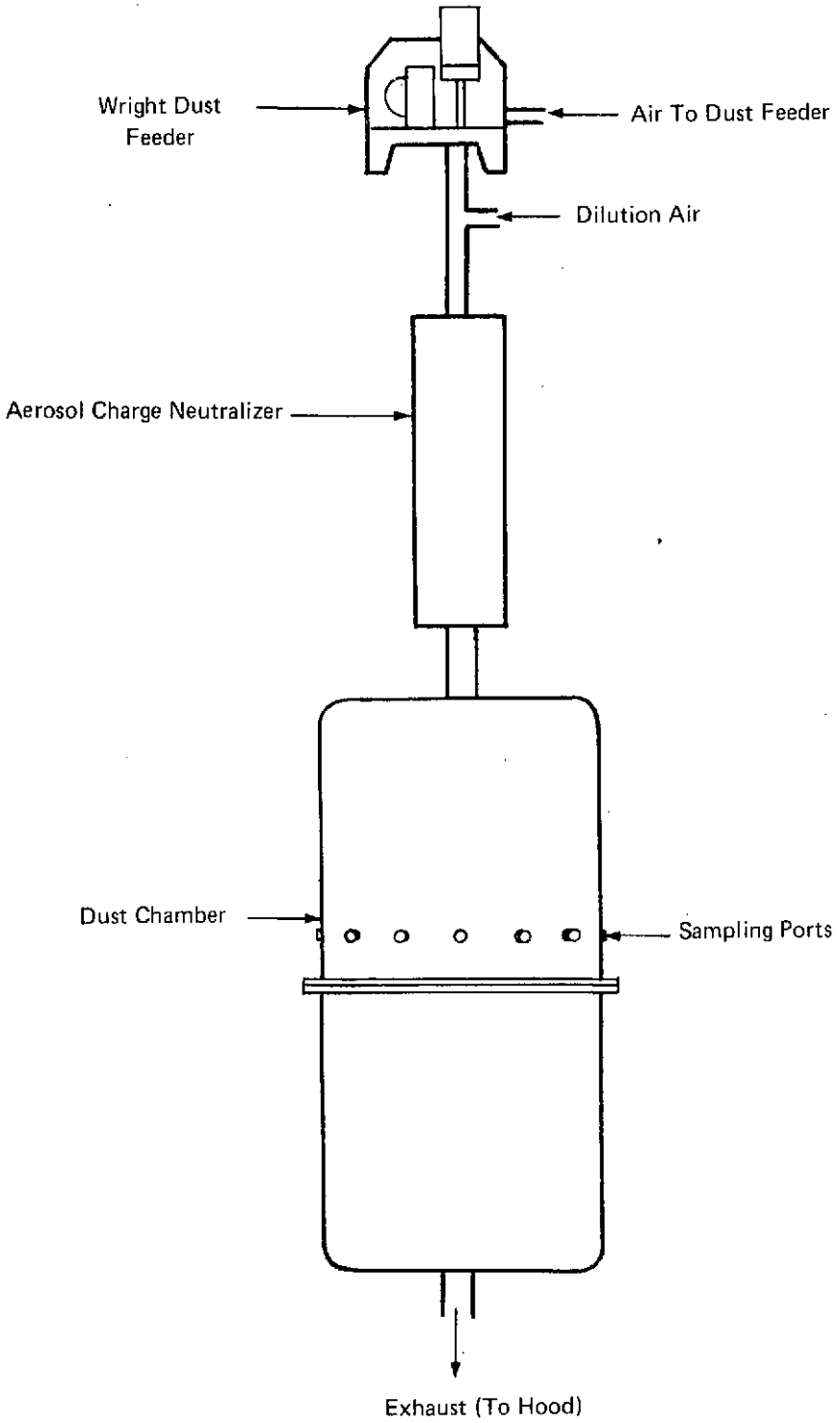

FIGURE 1 DUST GENERATION APPARATUS

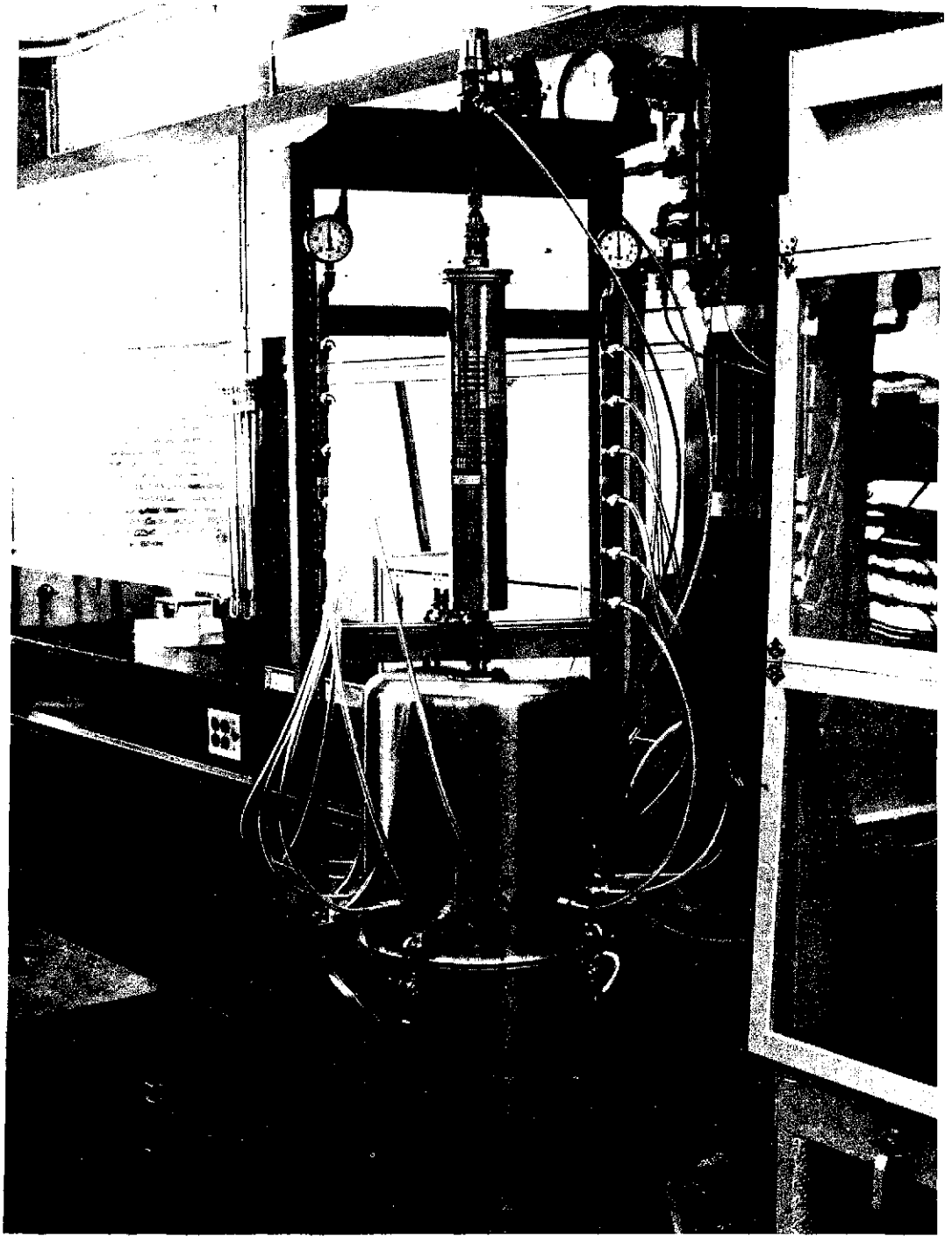

FIGURE 2 PHOTOGRAPH OF DUST GENERATION APPARATUS

by changing the gears in the drive mechanism to provide a wide range of dust concentrations.

A short distance downstream of the dust feeder there is an auxiliary port for introducing additional air for further dilution of the dust cloud. Normally a flow of 30 liters per minute is passed through the dust feeder itself and dilution air is added at the rate of 70 liters per minute. Air flow rates are read from calibrated rotameters. Compressed air is supplied to the apparatus from the house compressed air system. This air is dried by passing it through a silica gel bed and then through a high efficiency fibrous filter and a membrane filter to remove particulate matter.

Since dust particles may accumulate electrical charges in the dispersal process, the dispersed dust is passed through a charge neutralizer (Thermo-Systems Incorporated, Model 3045) before it is introduced into the dust chamber. The active element of the neutralizer is a 10 millicurie krypton-85 beta source. Beta rays from the krypton-85 interact with air molecules to generate both positive and negative ions. The ions become attached to the dust particles of opposite charge.

The dust chamber itself was constructed from two stainless steel stock pots. The pots are held together by three latches. An O-ring is used to provide an air-tight seal between the two pots. The chamber diameter is 14 inches and its height is 32 inches. Baffles were placed at the entrance and exit of the dust chamber to promote uniform distribution of the aerosol. The baffles are 5.75 inches in diameter, 0.015 inches thick, and are located approximately 1.5 inches away from the exit and entrance ports. The dust chamber is normally operated at a slight positive pressure with respect to the atmosphere (about 2 inches in H_2O). Effluent from the dust chamber is vented to a hood through a one-inch rubber hose.

Twelve sampling ports are located around the periphery of the dust chamber. The filter cassettes are mounted on the inside perimeter of the chamber and sample flow rate is controlled by critical orifices which are mounted outside the chamber on a U-shaped vacuum line (see Figure 2). The sampling rate is approximately 1.7 liters per minute.

For generation of the titanium dioxide dust atmosphere, TiO_2 powder was loaded into the dust container in a series of roughly one gram quantities. After each addition the powder was spread out to produce a layer of uniform thickness, and it was then compressed lightly (about 300 lbs) with a laboratory press. The concentration of the titanium dioxide in the chamber was controlled by proper adjustment of the dust holder advance rate, and the three test level concentrations were generated independently. Although 12 samples can be collected simultaneously, only six samples for each test level were analyzed. Samples were collected at 1.7 liters per minute for 60 minutes (102 liters). Since collection efficiency was found to be 1.00 ± 0.01, the concentrations in the generator and the "found" concentration were considered to be equal.

Collection Efficiency

The collection efficiency of the 37 mm Type AA Millipore filter for titanium dioxide dust was determined by collecting six filter samples at an air sample concentration of 29.5 mg/cu m. The physical layout of the filter series (front and backup) used for the six samples collected was such that the two filters were mounted back-to-back in contact with each other and supported by the backup pad. The average collection efficiency found was 100% when a test atmosphere containing 29.5 mg/cu m was sampled for 60 minutes (Table 1).

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$\overline{CV}_1 = 0.0627$ $\overline{CV}_2 = 0.0968$ $\overline{CV}_T = 0.112$

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

TABLE 1

Collection Efficiency: Titanium Dioxide, S385

mg Found			
Front	Backup	Total	% Collected in Front
3.06	ND	3.06	100%
3.17	ND	3.17	100%
3.16	ND	3.16	100%
3.04	ND	3.04	100%
3.03	ND	3.03	100%
3.07	ND	3.07	100%

Average Collection Efficiency..... 100%

ND - Not detectable; the detection limit was 0.1 mg in a 50 ml solution.

Data Sheet: Titanium Dioxide, S385

Analysis

Level	0.5S		1S			2S		
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
0.41	0.44	1.07	1.55	1.49	0.96	3.14	3.21	1.02
0.45	0.44	0.98	1.64	1.60	0.98	2.67	2.80	1.05
0.48	0.48	1.00	1.80	1.77	0.98	3.10	3.18	1.03
0.73	0.73	1.00	1.56	1.51	0.97	2.30	2.39	1.04
0.95	0.80	0.84	1.63	1.49	0.91	3.13	2.93	0.94
1.09	1.01	0.93	1.89	1.65	0.87	2.45	2.25	0.92
n =		6			6			6
mean		0.97			0.95			1.00
std dev		0.0780			0.0451			0.0555
CV_1		0.0804			0.0474			0.0555

$\overline{CV}_1$ 0.0627

$\overline{CV}_{A+\overline{DE}}$ 0.0677

1271<

Data Sheet: Titanium Dioxide, S385

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m
0.5S	1.054	105.7	9.97*
	0.874	102.6	8.52
	0.819	104.7	7.82
	0.834	104.3	8.00
	0.852	105.8	8.05
	0.856	106.6	8.03
		n = 5	
		mean	8.08
		std dev	0.260
		CV_2	0.0322
1S	1.029	106.3	9.68
	1.476	102.6	14.39
	1.538	104.1	14.77
	1.580	107.2	14.74
	1.310	105.8	12.38
	1.540	102.9	14.97
		n = 6	
		mean	13.49
		std dev	2.095
		CV_2	0.1553
2S	3.06	106.7	28.7
	3.17	102.6	30.9
	3.16	104.1	30.4
	3.04	107.2	28.4
	3.03	105.8	28.6
	3.07	102.9	29.8
		n = 6	
		mean	29.5
		std dev	1.050
		CV_2	0.0356
		$\overline{CV}_2$	0.0968

*These values excluded from statistical analysis

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