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333 Ravenswood Avenue
Menlo Park, California 94025

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National Institute for Occupational Safety and Health
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Cincinnati, Ohio 45226

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16. Abstracts

Industrial hygiene sampling and analytical methods were developed and validated under a follow-up research effort to develop measurement methods which failed to validate under the joint NIOSH/OSHA Standards Completion Program. This is the fourth set of 10 methods in an effort to develop methods for 130 substances. Monitoring methods for the following substances are included:

S214	Dinitrobenzene	S24	Diphenyl
S138	Butylamine	S228	Picric Acid
S158	2-Aminopyridine	S297	Pentachlorophenol
S181	Quinone	S105	Ethyl Chloride
S141	Diisopropylamine	S219	Nitroethane

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Chemical analysis
Sampling

*Dinitrobenzene	*Diphenyl
*Butylamine	*Picric Acid
*2-Aminopyridine	*Pentachlorophenol
*Quinone	*Ethyl Chloride
*Diisopropylamine	*Nitroethane

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Ten NIOSH Analytical Methods Set-4

A joint National Institute for Occupational Safety and Health (NIOSH)/Occupational Safety and Health Administration (OSHA) Standards Completion Program will complete standards for approximately 400 air contaminants presently listed in Tables Z-1, Z-2, and Z-3 of 29 CFR Part 1910.1000 by adding other requirements of a standard required under Section 6(b)(7) and 8(c)(3) of the Occupational Safety and Health Act of 1970 (PL 91-596). These completed standards will then contain, in addition to the permissible exposure limit given in 1910.1000, appropriate provisions requireing monitoring of worker exposure, engineering control, personal protection, employee training, medical surveillance, and record-keeping.

As a part of the Standards Completion Program, NIOSH engaged in a two-year study under contract CDC-99-74-45 to validate sampling and analytical procedures for use in monitoring worker exposure to substances listed in Tables Z-1, Z-2, and Z-3. One hundred seventy of the methods failed to validate under the guidelines of the SCP. One hundred thirty of the 170 methods which failed are being developed and validated in a follow-up project. These 10 methods have been validated and thus may be used for determining compliance with the standard or the need for control, for research, or whenever there is a need to measure airborne concentrations in the workplace. These analytical methods should bot be considered the only methods which may be used to evaluate worker exposure. Other methods meeting the accuracy requirements in the standard may also be used.

These analytical methods will be periodically modified as new developments in science and technology require.

Set 4

Dinitrobenzene
Butylamine
2-Aminopyridine
Quinone
Diisopropylamine
Diphenyl
Picric Acid
Pentachlorophenol
Ethyl Chloride
Nitroethane

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
Cincinnati, Ohio

May 1978

Dinitrobenzene
(all isomers)

Analyte:	Dinitrobenzene	Method No.:	S214
Matrix:	Air	Range:	0.42-2.4 mg/cu m
OSHA Standard:	1 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.091
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date:	4/15/77

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 10 ml of ethylene glycol to collect dinitrobenzene.

1.2 The filter and bubbler are disconnected. The filter is removed from the cassette holder and added to the bubbler flask. Five milliliters of methanol is added to the flask before analysis.

1.3 The resulting sample is analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.418-2.386 mg/cu m at an atmospheric temperature of 23°C and pressure of 758 mm Hg, using 90-liter samples.

2.2 The upper limit of the range of the method is dependent on the capacity of the mixed cellulose ester membrane filter connected in series to the midget bubbler and the capacity of the midget bubbler.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as dinitrobenzene at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.418-2.386 mg/cu m was 0.091. This value corresponds to a standard deviation of 0.09 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 2.4% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, storage stability, and collection efficiency were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.191 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer, supported by a stainless steel screen on a 37-mm two-piece cassette filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.

6.2 A glass midget bubbler containing 10 ml of ethylene glycol.

6.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a trap consisting of a second bubbler or impinger downstream from the midget bubbler.

6.4 Manometer.

6.5 Thermometer.

6.6 High pressure liquid chromatograph equipped with a 254-nm fixed wavelength uv detector and a sample injection valve with a 50-microliter external sample loop. The injection valve is fitted with a syringe filter to remove filter fibers which would eventually block the flow to the LC column.

6.7 Column (250 mm x 3-mm I.D. stainless steel) packed with Spherisorb ODS. The superficially porous packing material consists of spherical silica particles with a 5% bonded coating of octadecyl groups. This packing can be obtained from Spectra-Physics in Santa Clara, California.

6.8 An electronic integrator or some other suitable method for measuring peak areas.

6.9 Tweezers.

6.10 Microliter Syringes: 50 and 100-microliter.

6.11 Volumetric Flasks: Convenient sizes for preparing standard solutions.

6.12 Pipets: Convenient sizes for preparing standard solutions and 5- and 10-ml pipets for measuring the extraction medium.

6.13 Teflon tubing (15 cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

7.1 o-Dinitrobenzene, m-dinitrobenzene, and p-dinitrobenzene, reagent grade.

7.2 Ethylene glycol, reagent grade.

7.3 Methanol, distilled in glass.

7.4 2-Propanol, reagent grade.

7.5 Water, deionized and distilled.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a stainless steel screen. Secure the cassette holder together with tape or shrinkable band.

8.3.2 Pour 10 ml of ethylene glycol into each midget bubbler. Be sure that the bubbler frit is completely immersed in the ethylene glycol. If necessary adjust liquid level to cover the frit.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet of the midget bubbler to either the pump's inlet or the trap's inlet. When a trap is used, it is attached to the pump by tape or a holder. The outlet of the trap is connected by tubing to the pump's inlet. Material collected in the trap must never be returned to the midget bubbler. After sampling, discard the material collected in the trap. The bubbler must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.5 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.8 After sampling, disconnect the filter and bubbler. Remove the bubbler stem, and remove the filter from the filter cassette with clean tweezers and add it to the bubbler. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the

bubbler should be taped securely to prevent leakage during shipping. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of dinitrobenzene from the filter by vaporization may occur.

8.3.9 With each batch of ten samples submit one bubbler containing ethylene glycol and a blank filter from the same lot of filters and bubblers used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

8.3.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.4 Analysis of Samples

8.4.1 If the sample volume is less than 10 ml, add ethylene glycol until the volume reaches the 10-ml mark.

8.4.2 Add 5 ml of methanol to each sample and mix the solution by swirling. If the volume is not exactly 15.0 ml, make an appropriate correction in the calculation in Section 10.1. Allow the samples to stand for 2 hours before analysis.

8.4.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 2500 psi
Flow Rate: 1.9 ml/min
Mobile Phase: 20% methanol/80% water (V/V)
Detector: uv photometer at 254 nm
Capacity Ratio: 8.6

There are three isomers of dinitrobenzene. This method was validated using only the meta isomer, which is the predominant isomer in a mixture of isomers of dinitrobenzene (approximately 93% of the total as given in Reference 3).

Using the HPLC operating conditions above, the isomers can be eluted separately from the column. If more than one isomer is present in the sample, it is important that the HPLC conditions allow adequate separation of the isomers, since they must be quantitated independently. The response for each isomer should be determined.

8.4.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 50-microliter sample loop. Flush this loop thoroughly with the sample (300 microliters), and inject the sample.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.

9.1 Prepare a 2.25 mg/ml dinitrobenzene stock standard solution (for the isomer of interest) by dissolving 56.25 mg dinitrobenzene in 2-propanol and diluting to 25 ml in a volumetric flask.

9.2 From the above stock solution, appropriate aliquots are withdrawn and added to 10 ml ethylene glycol and 5 ml methanol. Prepare at least 5 working standards to cover the range of 0.013-0.40 mg/15 ml. This range is based on a 90-liter sample. Analyze samples as per Section 8.4.

9.3 Prepare a standard calibration curve by plotting concentration of dinitrobenzene in mg/15 ml versus peak area. A calibration curve should be prepared for each isomer of interest.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of ethylene glycol/methanol and the volume of sample injected is identical to the volume of the standards injected. If more than one isomer is present, combine the mg found for each isomer to give the total weight of dinitrobenzene in the sample.

10.2 A correction for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter

mg blank = mg found in blank filter

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of dinitrobenzene in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2) x 1000 (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

11. References

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

11.2 Backup Data Report for Dinitrobenzene, prepared under NIOSH Contract No. 210-76-0123.

11.3 March, J. Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, McGraw-Hill, New York (1968), 382.

Sampling Data Sheet No. S214

April 15, 1977

Substance

Dinitrobenzene (all isomers)

Standard

8-hour time-weighted average: 1 mg/cu m - skin

Analytical Method

A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 10 ml of ethylene glycol to collect dinitrobenzene. The filter and bubbler are disconnected, and the filter is removed from the cassette holder and added to the bubbler flask. Dinitrobenzene is analyzed by high pressure liquid chromatography. The method has been validated over the range of 0.418-2.386 mg/cu m for a 90-liter sample at 23°C and 758 mm Hg atmospheric temperature and pressure.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow rate can be determined accurately (±5%) at 1.5 liters per minute, a 37-mm two-piece cassette filter holder held together by tape or shrinkable band, and a 37-mm/0.8 micrometer cellulose ester membrane filter connected in series with a midget bubbler. The bubbler medium is reagent grade ethylene glycol, and it should be obtained from the supporting analytical laboratory. The filter is supported by a stainless steel screen. It is important that the screen be used rather than a backup pad, as dinitrobenzene vapors may be partially retained by the pad, and low results obtained. The pump can be protected from spillage or splashover by using a trap which is a second bubbler or impinger downstream of the midget bubbler. Teflon tubing (15 cm long x 7-mm I.D.) or Teflon plugs are needed for sealing the inlet and outlet of the bubbler stem before shipping.

Sample Size

A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

Sampling Procedure

1. Assemble the filter in the two-piece filter cassette holder and close firmly. Secure the cassette holder together with tape or a shrinkable band. Pour 10 ml of the ethylene glycol into each

bubbler. Be sure that the frit is completely immersed in the ethylene glycol. If necessary, adjust the liquid level to cover the frit.

2. Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet of the midget bubbler to either the pump's inlet or the trap's inlet. When a trap is used, it is attached to the pump by tape or a holder. The outlet of the trap is connected by tubing to the pump's inlet. Material collected in the trap must never be returned to the midget bubbler. After sampling, discard the material collected in the trap. The bubbler must be maintained in a vertical position during sampling.

3. Air being sampled should not pass through any hose or tubing before entering the filter cassette.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump used. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

5. After sampling, disconnect the filter and bubbler. Remove the bubbler stem, and remove the filter from the filter cassette with clean tweezers and add it to the bubbler. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of dinitrobenzene from the filter by vaporization may occur.

6. Carefully record the sample identity and all relevant sampling data such as sample flow rate and collection time.

7. With each batch of ten samples submit one midget bubbler containing 10 ml of ethylene glycol and a blank filter from the same lot of filters and bubblers used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

Special Consideration

When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Shipping Instructions

The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

Reference

Dinitrobenzene, NIOSH Method No. S214.

Backup Data Report No. S214
April 15, 1977

Substance: Dinitrobenzene (all isomers)

OSHA Standard: 1 mg/cu m - skin

Chemicals Used for Validation:
m-Dinitrobenzene, reagent grade from Fisher Chemical Co.
o-Dinitrobenzene, 99% pure from Aldrich Chemical Co.
p-Dinitrobenzene, reagent grade from Eastman Chemical Co.

General

The procedure for collection and analysis of air samples of dinitrobenzene is described in NIOSH Method No. S214. This method consists of collection of the sample on cellulose ester membrane filters connected in series to a backup bubbler containing 10 ml of ethylene glycol. The filter is added to the bubbler. Prior to analysis, five milliliters of methanol is added. The resulting solution is analyzed by high pressure liquid chromatography.

This method has been tested for a 90-liter air sample, using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) should be less than 25% at the OSHA standard level 95% of the time.

The protocol for validation of this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of dinitrobenzene to represent 90-liter air samples.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

Determine the collection efficiency of the collection media consisting of a cellulose ester membrane filter connected in series to a backup bubbler.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S214. The results of the analytical method recovery tests are in Table

S214-6. Only the meta isomer was used in the validation study, since it is the predominant isomer in a mixture of isomers of dinitrobenzene. Work was conducted on the separation of a mixture of the three isomers. The result of this work is presented below.

Using the HPLC operating conditions given in the method for dinitrobenzene, Method No. S214, the isomers were separated and eluted from the column at the following retention times:

Solvent	41.4 seconds
p-dinitrobenzene	322.2 seconds
m-dinitrobenzene	399.0 seconds
o-dinitrobenzene	484.2 seconds

The average HETP (height equivalent of a theoretical plate) value for the three isomers using the Spherisorb ODS column was 0.65 mm. The average theoretical plate number (N) for the column is 383.

The uv detector response is not the same for the three isomers. Good separation of the peaks is needed so areas can be measured quantitatively. The separation factor (alpha) may be calculated following the procedure described in Reference 2. For the two pairs of isomers, alpha was calculated to be as follows:

para-meta	1.27
meta-ortho	1.24

Adequate separation of two adjacent bands was quantitated by the resolution factor R_S. For this separation, the R_S factor was approximately 1.0 for both the para-meta and meta-ortho isomer pairs. When $R_S = 1.0$, the bands are well separated and relative band heights can be varied from 128/1 to 1/128 and quantitative accuracy of better than 3% can be obtained. The table below lists the detector response of the p- and o-isomers relative to the m-isomer, for the conditions listed in Method S214.

	Area Counts	Response Relative to m-Isomer
p-dinitrobenzene	9,895	0.74
m-dinitrobenzene	13,401	1.00
o-dinitrobenzene	3,558	0.27

Sampling and Analysis

Samples of m-dinitrobenzene in air were generated by the procedure described in Attachments A and B and collected as described in Method No. S214. The results of the sampling and analysis experiments are presented in Table S214-7.

A 10 g/liter solution of m-dinitrobenzene in 2-propanol was used in the aspiration system for the generation of dinitrobenzene. To obtain the desired concentration, a set of generation conditions were chosen, and 15-minute samples from the 2X chamber were collected and analyzed. The results of the analyses were used to determine the conditions necessary

to obtain the required concentration. When the desired concentration was reached, six samples were collected simultaneously each at the 2X, 1X, and 0.5X levels.

Samples were collected for 60 minutes at a flow rate of approximately 1.5 liters per minute.

Collection Efficiency

Collection efficiency tests were conducted at 4.6 mg/cu m (as determined by analysis of the collected samples). The samples were collected using a filter connected in series to two backup midget bubblers. The first bubbler contained 10 ml of ethylene glycol, and the second bubbler contained 10 ml of methanol. The generation conditions used were the same as described under the Sampling and Analysis Section. Samples were collected for 60 minutes at a flow rate of approximately 1.5 liters per minute. The results of the collection efficiency tests are presented in Table S214-1.

Table S214-1

Collection Efficiency Tests

mg found in filter and first bubbler	mg found in second bubbler	Collection Efficiency
0.388	N.D.**	1.00
0.367	N.D.**	1.00
0.418	N.D.**	1.00
0.393	N.D.**	1.00
0.399	N.D.**	1.00
0.403	N.D.**	1.00

** N.D. = Not detected at a detection limit of 0.003 mg.

Storage Stability

A storage stability test was conducted to assess whether dinitrobenzene could be successfully stored in solution for one week after collection. Six samples were collected at 1X the OSHA standard level at a concentration of 1.191 mg/cu m (as determined by the independent method). The samples were collected for 60 minutes at an average flow rate of approximately 1.5 liters per minute. An aliquot was analyzed immediately, and the remainder of the solution was stored for one week. After one week, an aliquot was analyzed. The samples were analyzed as described in Method S214. The results of the storage stability test are presented in Table S214-2.

Table S214-2

Storage Stability Tests

Samples Analyzed Immediately mg/cu m	Samples Analyzed After One Week mg/cu m
1.007	0.996
0.963	0.954
1.188	1.174
1.146	1.185
1.015	1.039
1.158	1.175
mean 1.079	1.087
std dev 0.095	0.103
CV 0.088	0.095

The criterion for acceptance was that the mean of the six samples stored at room temperature for seven days should be ±10% of the mean of the samples at the beginning of the storage period. The two means in the above table compare within 0.74%; thus, the storage stability was adequate.

An additional storage stability test was conducted. The filters in this experiment were left in the filter cassettes for one week before they were added to the midget bubblers. Three samples were collected at 1X the OSHA standard level. After one week the filter was added to the bubbler, and the samples were analyzed as described in Method No. S214. The results are presented in Table S214-3.

Table S214-3

Storage Stability in Filter Cassettes

	No. of Samples	mg/cu m found (mean)	Std Dev	CV
Samples Analyzed Immediately (from Table S214-2)	6	1.079	0.095	0.088
Samples Analyzed After One Week--Filters Stored in Cassettes	3	1.030	0.066	0.064

These results compare within 5%. However, it is recommended that the filter be transferred to the bubbler solution immediately after sampling, since losses may occur if the filters are subjected to high temperatures.

Discussion

An experiment was conducted to determine the vapor/particulate ratio of

dinitrotoluene (see Backup Data Report No. S215, Reference 3). The results of this experiment showed that dinitrotoluene is present as both particulate and vapor. It was assumed that dinitrobenzene would also be present as both particulate and vapor.

Independent Method

An independent method of measuring the concentration of dinitrobenzene was conducted so that the results from the validated method could be compared. For this method, samples were collected on a glass fiber filter connected in series to a midget bubbler containing 10 ml of 2-propanol. After collection, the solution in the bubbler was brought up to 15 ml with 2-propanol and the filters were added to the bubblers to extract the particulate dinitrobenzene. The test atmosphere was generated from a 10 g/liter solution of dinitrobenzene in 2-propanol, and samples were collected for 60 minutes at an average flow rate of 1.5 liters per minute. These samples were analyzed spectrophotometrically at 2350 Å. The Millipore Type AA filter could not be used, because the 2-propanol extracted interfering materials from it.

The concentrations of dinitrobenzene found using the independent method at the three generated levels are given in Table S214-5.

Table S214-5

0.5X	0.418 mg/cu m
1X	1.191 mg/cu m
2X	2.386 mg/cu m

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 4. A summary is given in Attachment C.

The precision of the analytical method was assessed using the data in Table S214-6. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.022.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S214-7 and the results from the storage stability and collection efficiency tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from test atmospheres is 0.076.

Confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described above.

The total Coefficient of Variation ($\overline{CV}_T$) is 0.091.

Table S214-6

Data Sheet: m-Dinitrobenzene

Analysis

Level	0.5X			1X			2X	
mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
0.0450	0.0447	0.993	0.0900	0.0910	1.011	0.1800	0.1733	0.963
0.0450	0.0436	0.969	0.0900	0.0906	1.007	0.1800	0.1826	1.014
0.0450	0.0452	1.004	0.0900	0.0879	0.977	0.1800	0.1831	1.017
0.0450	0.0454	1.009	0.0900	0.0911	1.012	0.1800	0.1882	1.046
0.0450	0.0450	1.000	0.0900	0.0887	0.986	0.1800	0.1841	1.023
0.0450	0.0440	0.978	0.0900	0.0870	0.967	0.1800	0.1881	1.045
n =		6			6			6
mean		0.992			0.993			1.018
std dev		0.016			0.019			0.030
CV_1		0.016			0.019			0.029

$\overline{CV_1}$ 0.022

$\overline{CV_{A+\overline{AMR}}}$ 0.024

Table S214-7

Data Sheet: m-Dinitrobenzene

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m*	mg/cu m	Recovery
0.5X	0.0358	91.2	0.393	0.418	
	0.0393	90.6	0.434	0.418	
	0.0338	91.2	0.371	0.418	
	0.0393	92.5	0.425	0.418	
	0.0444	91.2	0.487	0.418	
	0.0380	89.3	0.426	0.418	
		n = 6			
		mean	0.423		101.2
		std dev	0.040		
		CV_2	0.095		
1X	0.0918	91.2	1.007	1.191	
	0.0916	95.1	0.963	1.191	
	0.1061	89.3	1.188	1.191	
	0.1045	91.2	1.146	1.191	
	0.0972	95.8	1.015	1.191	
	0.1041	89.9	1.158	1.191	
		n = 6			
		mean	1.079		90.6
		std dev	0.095		
		CV_2	0.088		
2X	0.2214	93.2	2.376	2.386	
	0.2172	91.9	2.363	2.386	
	0.2224	91.2	2.439	2.386	
	0.2144	91.9	2.333	2.386	
	0.2204	89.9	2.452	2.386	
	0.2280	90.6	2.517	2.386	
		n = 6			
		mean	2.413		101.1
		std dev	0.068		
$\overline{CV}_2$ 0.076		CV_2	0.028		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

2. Snyder, L. R. and J. J. Kirkland, Introduction to Modern Liquid Chromatography, John Wiley and Sons, New York, (1974), 17-90.

3. Backup Data Report No. S215 for Dinitrotoluene, prepared under NIOSH Contract 210-76-0123.

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

Attachment A

Generation of Organic Particulates

Test atmospheres of organic particulates are generated by an aspiration/spray-dry technique. The aerosol generation system consists of a fluid aspirator, an impactor, a cyclone and a mixing chamber where solvent evaporates from the aerosol droplets. Several different aspirators are available.

Aerosols are produced by atomization of a solution of the analyte in a suitable solvent. Larger particles of atomized material are removed by impaction of the droplets on the walls of the vessel; all particles with diameters greater than two microns are removed by passing the aerosol through a cyclone.

The remaining droplets are mixed with solvent-free air in the mixing chamber. The residence time in the mixing chamber is sufficient for solvent evaporation to occur.

Generation of aerosols at the desired concentration is accomplished by adjusting the grams of analyte per liter of solvent and/or the flow of air through the aspirator and the amount of primary dilution air.

Attachment B

Generation of Test Atmospheres

The system for generating and collecting samples of vapor, inorganic/organic particulate, dusts, and fumes 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. A schematic of the generation system and associated components is presented in Figure 1.

The generation system is large enough to be used for polydispersed aerosols as well as for gases and vapors. The primary dilution chamber is 48 inches by 4 inches and may handle air flows up to 400 liters/minute. The large volume dilution chamber is important for several reasons. Even at high air flow rates, the velocity of particles is low to allow complete solvent evaporation in the generation of aerosols. The air velocity is also low enough to avoid impaction on the walls while great enough to prevent particle diffusion to the walls. For these same reasons, the sample rationing system is only 1 inch in diameter and handles a flow of only 52 liters/minute. Gravitational settling is avoided by maintaining a sufficient air velocity.

The sampling cones for the three chambers are 6-inch I.D. at the base (point of sample collection) and narrow to 1-inch I.D. at the point of attachment to the sample rationing system. A constant total air flow of 26 liters/minute through each cone causes a gradual reduction in aerosol velocity toward the point of sample collection. The air velocity at the collection point is 2.4 cm/sec. Isokinetic sampling is not attempted here since sampling will not be done in this manner in the field.

All portions of the generation system that come in contact with the test atmosphere are constructed of stainless steel or Teflon to avoid any contamination problems. Sections of the generation system at which dilution air is added are constructed such that incoming air forms a "high-velocity sheath" around the air/analyte mixture that is to be diluted. This sheath serves two functions. The dilution air sheath becomes increasingly less coherent and stable as it moves downstream of its point of entrance and hence is turbulently mixed with air/analyte test atmosphere. At the point of entrance of the dilution air stream, a Venturi effect accelerates the air/analyte mixture to a high velocity. The dilution air sheath also prevents interaction of the accelerated air/analyte stream with the walls of the chamber, thus eliminating a large source of aerosol loss by impaction.

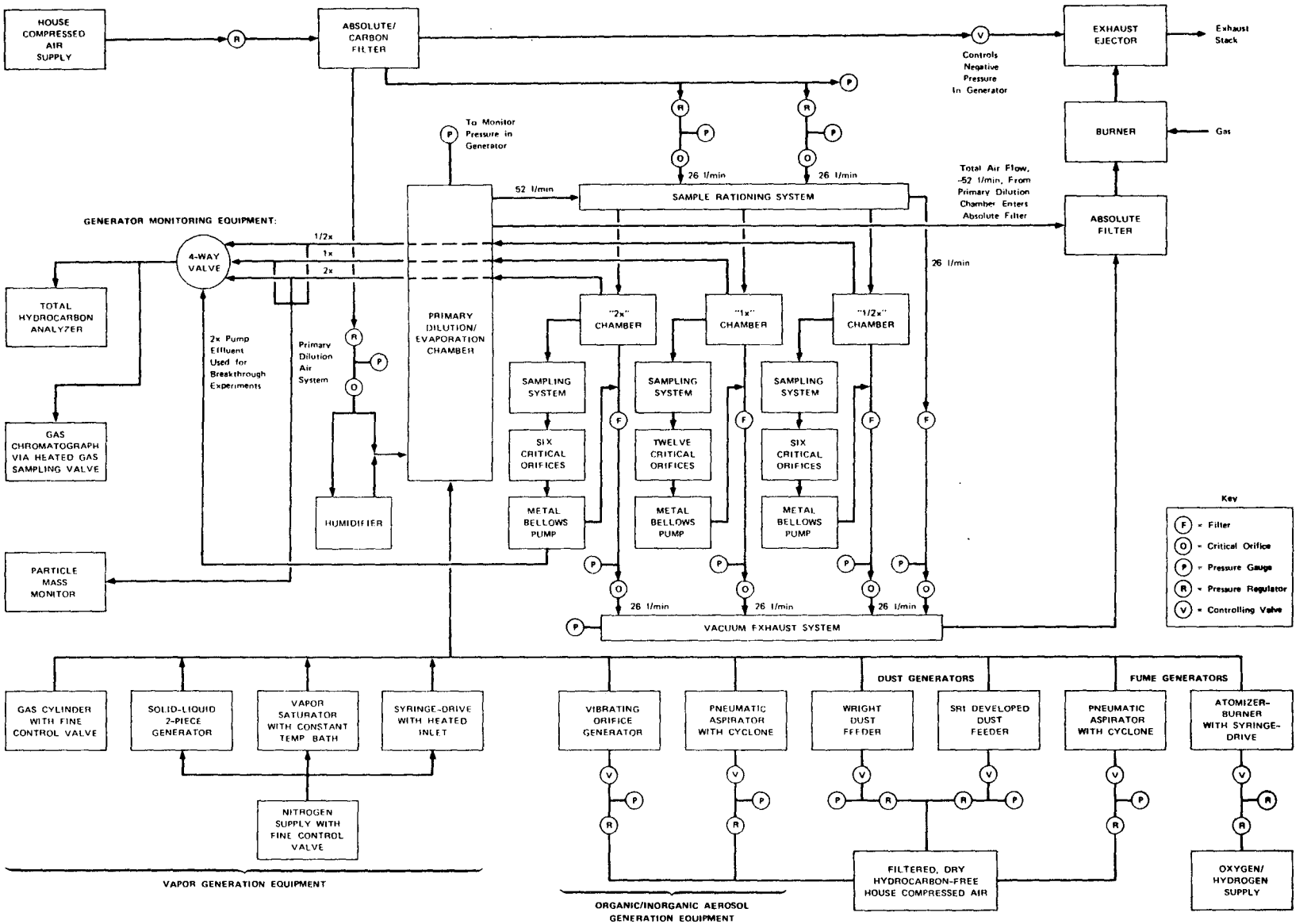


FIGURE S214-B1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

The system being used to generate the initial concentrations of vapor, gas, or particulate is interfaced with the dilution apparatus at the primary dilution chamber. The output of the generator is diluted with the appropriate amount of air to obtain a concentration 2X the OSHA standard. Of the total amount of material generated at the 2X level, a flow of 52 liters/minute enters the rationing system. Under control of a vacuum exhaust orifice, material at the 2X level enters the first sampling chamber at a rate of 26 liters/minute. Downstream of the entrance to the first sampling chamber, dilution air is added (via a critical orifice) at a rate of 26 liters/minute. Thus, the flow of material at the 2X level that did not enter the first sampling chamber (26 liters/minute) is diluted with air at a flow rate of 26 liters/minute to a final concentration of 1X the OSHA level. Analyte at the 1X level then enters the second sampling chamber at a rate of 26 liters/minute. The remaining flow, 26 liters/minute, is diluted again with air at 26 liters/minute to achieve 0.5X the OSHA standard level. The analyte/air mixture at the 0.5X level is drawn into the third sampling chamber at 26 liters/minute. The remaining material in the rationing system not drawn into the sampling chambers is removed at a rate of 26 liters/minute by the fourth critical orifice in the vacuum exhaust system. This removal of test atmosphere volumes and addition of measured volumes of air thus achieves serial dilutions to 1X and 0.5X the OSHA standard level.

The dilution ratios from chamber to chamber can also be varied by simply changing the amount of dilution air that is added. This is particularly advantageous in generating aerosols, where wall deposition of particles in the rationing system can be offset by changing the rate of addition of dilution air.

The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected simultaneously. A metal bellows vacuum pump is used for sampling from each chamber. Separate critical flow orifices are used for each sample. Air taken from the chamber during sampling is returned via the sampling pump exhaust line to the chamber outlet line, thus preserving the proper air flows during the time of sampling. The sampling rate therefore does not affect the concentration of material in any of the chambers.

The entire system is maintained at 1-inch water vacuum to prevent toxic materials from escaping into the laboratory. All exhaust air streams (from the vacuum exhaust system and excess from the primary dilution chamber) are fed into a combustion chamber where all toxic materials present are burned before entering the atmosphere.

Attachment C

Summary of Statistical Terms and Formulas

The statistical analysis employed in this program has been provided by NIOSH. The evaluation of the limits and guidelines are discussed in memoranda from Busch (Reference 1). 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 0.5X, 1X, and 2X the OSHA standard level.

CV_2 - Coefficient of Variation for the six generated samples at each of the 0.5X, 1X, and 2X the 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 of 0.5X, 1X, and 2X the OSHA standard level. The mathematical equation is express 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.

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

$\overline{CV}_2$ - 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.

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

$\overline{CV}_P$ - 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.

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

or:

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

Grubbs' 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:

$$B_{1'} = \frac{x - \bar{x}}{s} \quad \text{or} \quad \frac{\bar{x} - x}{s}$$

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 Coefficients of Variation

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 0.5X, 1X, and 2X the OSHA standard level). The following equation for chi squared, with n-1 degrees of freedom, was used:

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

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, 4.....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

1. 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 1/6/76 and 11/8/74.

n-Butylamine

Analyte:	n-Butylamine	Method No.:	S138
Matrix:	Air	Range:	8.1 - 35.5 mg/cu m
OSHA Standard:	5 ppm (15 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.092
Procedure:	Adsorption on sulfuric acid-treated silica gel, desorption with 50% methanol, GC/FID	Validation Date:	7/8/77

1. Principle of the Method

1.1 A known volume of air is drawn through a sulfuric acid-treated silica gel tube to trap the organic vapors present. The sampling tube consists of front and backup adsorbing sections.

1.2 The treated silica gel in each section is transferred to a vial and the n-butylamine is desorbed with 50% methanol and analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 8.09-35.5 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 769 mm Hg using a 15-liter sample volume. When an atmosphere at 90% relative humidity containing 34.4 mg/cu m of n-butylamine was sampled at 0.8 liter per minute, no breakthrough was observed after 240 minutes (190 liters); the capacity of the acid-treated silica gel is at least 6.5 mg under the conditions of these breakthrough studies.

2.2 This method is capable of measuring much smaller amounts of n-butylamine if the desorption efficiency is adequate. Desorption efficiency must be determined over the concentration range of interest.

2.3 The upper limit of the range of the method is dependent on the adsorptive capacity of the treated silica gel tube. This capacity can vary with the concentrations of analyte and other substances in the air.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.09-35.5 mg/cu m was 0.0923. This value corresponds to a 1.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.6% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

4.3 The data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The sorbent tubes are analyzed by means of a quick, instrumental method.

5.2 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will effect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated with one tube only.

5.3 This method is limited to sampling atmospheres where the relative humidity is less than 60%.

6. Apparatus

6.1 Sampling Equipment

6.1.1 Sampling Pump. A calibrated personal sampling pump whose flow can be determined to within ±5% at the recommended flow rate of 1.0 liter per minute.

6.1.2 Sampling Tubes. The sampling tube consists of a glass tube with both ends flame-sealed, 7 cm long with a 6-mm O.D. and 4-mm I.D., containing two sections of 20/40 mesh sulfuric acid-treated silica gel. The front adsorbing section contains 150 mg of treated silica gel, the backup section, 75 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the back-up section. Since the pressure drop across the tube must be less than 25 mm Hg at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

The sulfuric acid-treated silica gel may be prepared as follows: A known amount of 20/40 mesh silica gel is placed in a drying oven at 125°C for one hour to activate the silica gel. The gel is then cooled to a constant weight, W. Reagent grade concentrated sulfuric acid is added dropwise by means of a disposable pipet to 1.25 W, or 25% by weight acid. A glass stirring rod is used to more evenly distribute the sulfuric acid. The treated silica gel is then returned to the drying oven for one hour with intermittent mixing. The treated silica gel should be stored in an airtight container.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.1.6 Hygrometer or other suitable device for measuring relative humidity.

6.2 Gas chromatograph with a flame ionization detector.

6.3 Column (6 ft x 1/4-in O.D. x 2-mm I.D. glass), packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Sample containers, 2-mL with Teflon-lined caps.

6.6 Microliter syringes, 10- and 500-microliter and other convenient sizes for making standards and for taking sample aliquots for dilution.

6.7 Pipets, 1-mL, delivery type.

6.8 Volumetric flasks, 1- and 10-mL, or convenient sizes for making standard solutions.

7. Reagents

7.1 50% methanol (50 parts methanol + 50 parts water).

7.2 1.0 N potassium hydroxide.

7.3 n-Butylamine, reagent grade.

7.4 n-Butyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in 1.0 N potassium hydroxide.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling tube in the line; the tube is described in Section 6.1.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

Note: This method is limited to sampling atmospheres where relative humidity is less than 60%.

8.3.1 Immediately before sampling, break the two ends of the treated silica gel tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The section containing 75 mg of treated silica gel is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The treated silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the treated silica gel.

8.3.5 A sample size of 15 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 15 minutes. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The treated silica gel tube should be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples, submit one treated silica gel tube which has been handled in the same manner as the sample tubes (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped, treated silica gel tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each tube is scored with a file in front of the first section of treated silica gel and broken open. The glass wool is removed and discarded. The treated silica gel in the front 150-mg section is transferred to a 2-mL screw-capped sample container. The separating section of glass wool is removed and discarded. The second 75-mg section is transferred to another container. These two sections are analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 1 mL of 50% methanol is pipetted into each sample container. Desorption should be done for 2 hours. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 Neutralization of Sample. Withdraw a 500-microliter aliquot of the supernatant liquid and transfer to another 2-mL vial. Add 500 microliters of 1.0 N potassium hydroxide solution.

Note: If the internal standard method is used, add the internal standard solution made up in 1.0 N potassium hydroxide.

8.4.4 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 20 mL/min (60 psig) Nitrogen carrier gas flow

2. 30 mL/min (25 psig) Hydrogen gas flow to detector
3. 300 mL/min (60 psig) Air flow to detector
4. 175°C injector temperature
5. 195°C manifold temperature (detector)
6. 90°C column temperature

A retention time of approximately ten minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately 22 minutes.

8.4.5 A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.6 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as described in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of sulfuric acid-treated silica gel to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of treated silica gel used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at the OSHA standard level.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of n-butylamine found in the samples.

The analytical samples are prepared as follows: 150 mg of acid-treated silica gel is measured into a 2-mL screw-capped vial. This treated silica gel must be from the same batch as that used in obtaining the samples. A known amount of a solution of n-butylamine in water (spiking solution) is injected directly into the treated silica gel by means of a microliter syringe. Adjust the

concentration of the spiking solution such that no more than a 10-µL aliquot is used to prepare the analytical samples.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) were prepared by adding an amount of n-butylamine equivalent to that present in a 15-liter sample at the selected level. A stock solution containing 55.5 milligrams of n-butylamine per milliliter of water was prepared. Two, four and eight microliter aliquots of the solution were added to the treated silica gel tubes to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand at least overnight to assure complete adsorption of the analyte onto the treated silica gel. A parallel blank tube was treated in the same manner except that no sample was added to it.

8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 1 mL of 50% methanol. A 500-microliter aliquot is transferred and treated with 500 microliters 1.0 N potassium hydroxide. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare all sample solutions using 500 microliters of 1.0 N potassium hydroxide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in µg recovered from the tube divided by the weight in µg added to the tube, or

$$D.E. = \frac{\text{Average Weight (µg) recovered - Blank (µg)}}{\text{Weight (µg) added}}$$

The desorption efficiency may be dependent on the amount of n-butylamine collected on the treated silica gel. Plot the desorption efficiency versus weight of n-butylamine found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

9.1 Solutions of n-butylamine should be prepared over the appropriate concentration range. The spiking solution described in Section 8.5.2 should be used with the same syringe used in the preparation

of the samples. Two, four and eight microliter aliquots are added to 1 mL of 50% methanol in 2-mL vials. A 500-microliter aliquot of each standard solution is transferred to a second 2-mL vial and treated with 500 microliters 1.0 N potassium hydroxide.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area against sample concentration in µg/mL.

For the internal standard method, use 1.0 N potassium hydroxide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 65% of the concentration at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in µg/mL.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample:

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in front (150 mg) sample section

µg blank = µg found in front (150 mg) blank section

A similar procedure is followed for the backup (75 mg) section.

10.3 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Weight (Front Section)}}{DE}$$

10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected µg (see Section 10.3)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{73.14} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) or air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

73.14 = molecular weight of n-butylamine

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Back Data Report for n-Butylamine, No. S138, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S138
July 8, 1977

Substance

n-Butylamine

Standard

Ceiling: 5 ppm (15 mg/cu m)

Analytical Method

A known volume of air is drawn through a sulfuric acid-treated silica gel tube to trap the n-butylamine vapors present. The n-butylamine is desorbed from the treated silica gel with 50% methanol, and the sample is analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 8.09-35.5 mg/cu m for a 15-liter sample at 24°C and 759.4 mm Hg atmospheric temperature and pressure. It should be emphasized that this method is not valid when the relative humidity of the atmosphere being sampled is greater than 60%.

Sampling Equipment

The sampling equipment needed consists of a sulfuric acid-treated silica gel sampling tube and a personal sampling pump calibrated with a representative silica gel tube in the line. The pump flow rate should be determined accurately, ± 5%, at 1.0 liter per minute. A suitable tube holder should be used to protect the worker from the sharp edges of the glass sampling tube.

The silica gel tube used to collect the sample consists of a glass tube flame sealed at both ends, 7-cm long with a 6-mm O.D. and a 4-mm I.D., packed with two sections of 20/40 mesh silica gel treated with sulfuric acid. The two sections include a front section containing 150 mg of treated silica gel and a backup section containing 75 mg. The two sections are separated by a plug of silylated glass wool and both the inlet and outlet ends of the tube are plugged with silylated glass wool. The pressure drop across the tube must be less than 25 mm Hg at a flow rate of 1 liter per minute.

The treated silica gel may be prepared as follows: A known amount of 20/40 mesh silica gel is placed in a drying oven at 125°C for one hour to activate the silica gel. The gel is then cooled to constant weight, W. Reagent grade concentrated sulfuric acid is added dropwise by means of a disposable pipet to 1.25W, or 25% by weight acid. A glass stirring rod is used to more evenly distribute the sulfuric acid. The treated silica gel is then returned to the drying oven for one hour with intermittent mixing. The treated silica gel should be stored in an airtight container.

Sample Size

A sample size of 15 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 15 minutes.

Sampling Procedure

1. Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes.

2. The section containing 75 mg of treated silica gel is used as a back-up and should be positioned nearer the sampling pump. The silica gel tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the front section of the treated silica gel tube.

4. Set the pump flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. The treated silica gel tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

6. One treated silica gel tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every batch of ten samples.

7. In addition, several unused and sealed treated silica gel tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples, because desorption efficiency may vary from one batch of treated silica gel to another.

Special Considerations

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Due to the high resistance of the treated silica gel tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without first fully recharging the battery.

3. This method is limited to sampling atmospheres where the relative humidity is less than 60%.

Shipping Instructions

Capped silica gel tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

Reference

n-Butylamine, NIOSH Method No. S138.

Backup Data Report No. S138
July 8, 1977

Substance: n-Butylamine

OSHA Standard: 5 ppm (15 mg/cu m) - Ceiling

Chemical Used for Validation: n-Butylamine, 98.9%, Fisher Chemical Company

General Considerations

The method for n-butylamine has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ± 10% and the $\overline{CV}_T$ of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for n-butylamine consisted of the following experimental studies:

- Determination of the breakthrough capacity of sulfuric acid-treated silica gel at high relative humidities,
- Analysis of a total of eighteen (six samples at each of the three test levels--0.5, 1 and 2X the OSHA standard) spiked with the appropriate amount of n-butylamine to represent a sample volume equal to 15 liters,
- Analysis of a total of eighteen samples collected from dynamically generated test atmospheres (six samples at each of the three test levels--0.5, 1 and 2X the OSHA standard) for the same sample volume as above,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following appropriate sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Development of Analytical Method

Based on recommendations in the n-Butylamine Failure Report (Reference 3) and on the success reported by LASL for hydrazine (Reference 4), experiments were conducted to examine the efficiency of sulfuric acid-treated silica gel for the collection of n-butylamine vapors. The method used to prepare the silica gel was adapted with slight modifications from the method described by LASL. A known amount of 20/40 mesh silica gel, supplied by SKC, Inc., Pittsburgh, Pa., was activated in a drying oven at 125°C for one hour. The silica gel was then cooled to constant weight, W. Reagent grade concentrated sulfuric acid was added dropwise by means of a disposable pipet to 1.25W or 25% by weight acid. A glass stirring rod was used to mix the treated silica gel to more evenly distribute the sulfuric acid. The treated silica gel was then returned to the drying oven for one hour with intermittent mixing. The treated silica gel was stored in an airtight container.

Experiments to determine a suitable eluting solvent were conducted first. The results are shown in Table S138-1. Aliquots of a spiking solution of n-butylamine in water were added to 150 mg of sulfuric acid-treated silica gel in 2-mL vials. One mL of the desorbing solvent was added to the treated silica gel and allowed to desorb for two hours. A 500-microliter aliquot of the solvent was carefully transferred to another vial. This acidic extract was treated with 500 microliters of 1.0 N potassium hydroxide to release the free amine. A 5-microliter aliquot of the resulting basic solution was injected into the gas chromatograph. Based on the results shown in Table S138-1, 50% methanol was used for all subsequent desorption experiments.

Both concentrated sulfuric acid and silica gel are well-known desiccants. The question arose concerning the possible effects of sampling in a humid environment with sulfuric acid-treated silica gel. Table S138-2 summarizes experiments conducted with diisopropylamine to examine this question. Based on the results of these experiments, collection of n-butylamine on sulfuric acid-treated silica gel is limited to atmospheres where the relative humidity is less than 60%.

Principle of the Method

The method validated for the analysis of n-butylamine in air is based on collection on sulfuric acid-treated silica gel, desorption with 50% methanol, and analysis of the resulting solution by gas chromatography with a flame ionization detector. A sample size of 15 liters is recommended. Do not use this method to sample atmospheres where the relative humidity is greater than 60%.

Analysis

The general approach used and details of the equipment and instruments used for the analysis are described in Attachment A.

Table S138-1

Determination of Desorption Efficiency
with Various Solvents

(150 mg sulfuric acid-treated silica gel)

Solvent	Test Level	µg Added	µg Found	Average Desorption Efficiency*
Distilled Water	0.5S	111.0	56.6	0.510
	1S	222.0	122.9	0.554
	2S	444	294.4	0.663
10% Methanol	0.5S	111.0	69.3	0.624
	1S	222.0	143.0	0.644
	2S	444	305	0.687
50% Methanol	0.5S	88.8	81.9	0.922
	1S	177.6	161.4	0.909
	2S	355	324	0.913

* Average desorption efficiencies based on the analysis of three samples at each level.

Table S138-2

Data Sheet: Diisopropylamine

The Effect of Relative Humidity on Recovery

Experiment A: Samples desorbed in 1 mL 50% MeOH

Level	% Relative Humidity	----mg/cu m---- Found*	Taken	Recovery	Difference
0.5S	Dry	6.80	8.29	0.820	0.064
	36	6.38	8.44	0.756	
1S	Dry	15.55	18.21	0.854	0.068
	62	14.59	18.56	0.786	
2S	Dry	33.7	36.5	0.923	0.394
	73	19.68	37.2	0.529	

*Uncorrected for desorption efficiency in order to maintain a basis for comparison.

Experiment B: Samples desorbed in 2 mL to volume 50% MeOH

Level	% Relative Humidity	----mg/cu m---- Found*	Taken	Recovery	Difference
0.5S	Dry	6.55	8.44	0.776	0.080
	45	5.83	8.38	0.696	
1S	Dry	16.08	18.56	0.866	0.117
	65	13.79	18.41	0.749	
2S	Dry	33.1	37.2	0.890	0.373
	80	19.09	36.9	0.517Δ	

* Uncorrected for desorption efficiency.

Δ CV > 0.1

A detailed description of the procedure for analysis, the preparation of analytical samples for the determination of desorption efficiency, and the preparation of calibration standards are given in NIOSH Method No. S138 (Reference 5).

The reliability of the analytical method tested was based on the analysis of eighteen analytical samples. These samples were prepared by spiking 150 mg of acid-treated silica gel with known aliquots of n-butylamine in water. The aliquots (two, four, eight microliters) added contained respectively 111, 222 and 444 micrograms of n-butylamine representing the equivalent of a 15-liter air sample at 0.5, 1, and 2X the OSHA standard.

The data for the full set of eighteen analytical samples are shown in Table S138-3.

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachment B. A steady stream of n-butylamine was delivered via a calibrated syringe drive at a rate of 3.69 mg/min to a dry air stream flowing at a rate of 0.1039 cu m/min. Due to the high reactivity of n-butylamine with the stainless steel syringe needle, the syringe drive was connected directly to the generation equipment by means of a small piece of Teflon tubing. Using this approach, a reproducible and steady stream of n-butylamine vapor was produced in the test chamber. The three sample lines were maintained at measured dilution ratios of 0.228, 0.489, and 1.000 to produce the 0.5, 1, and 2X OSHA standard test levels. The delivery rate of the n-butylamine was determined by calibrating the syringe drive as described in Attachment C. The data are shown in the section on Independent Method of Verifying Generator Concentration.

The samples were collected using tubes packed with 150 mg of 20/40 mesh silica gel treated with sulfuric acid, described in Section 6.1.2 of NIOSH Method No. S138. Twenty-four samples were collected simultaneously at 1.0 liter per minute for 15 minutes (15 liters). Eighteen samples, six at each of the three test levels, were analyzed as described in Section 8.4 of NIOSH Method No. S138; the backup sections of the samples collected at 2X the OSHA standard level were analyzed similarly. The six remaining samples were stored and analyzed after seven days.

The data obtained for the eighteen one-day-old samples are shown in Table S138-4. It is also noted that no trace of n-butylamine was found in the backup sections of the tubes.

Storage Stability and Migration Studies

Studies were done to assess the stability of n-butylamine samples upon storage for one week at atmospheric conditions. For these studies, six stored samples at the OSHA standard level were analyzed and the results compared with the data for six OSHA standard level samples analyzed

Table S138-3

Data Sheet: n-Butylamine

(150 mg sulfuric acid treated silica gel, samples stored one day)

Analysis

Level	0.5S			1S			2S	
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
111.0	105.2	0.948	222.0	209.2	0.942	444	403	0.908
111.0	86.9	0.783	222.0	206.0	0.928	444	435	0.980
111.0	95.1	0.857	222.0	205.6	0.926	444	438	0.986
111.0	97.0	0.874	222.0	194.6	0.877	444	414	0.932
111.0	105.2	0.948	222.0	206.5	0.930	444	414	0.932
111.0	104.5	0.941	222.0	206.9	0.932	444	421	0.948
n =		6			6			6
mean		0.892			0.923			0.948
std dev		0.0665			0.02298			0.0303
CV_1		0.0746			0.02490			0.0320

$\overline{CV_1}$ 0.0490

$\overline{CV_{A+\overline{DE}}}$ 0.0529

Table S138-4

Data Sheet: n-Butylamine
Sampling and Analysis

(150 mg sulfuric acid-treated silica gel; samples stored one day)

Test Level	Found				Taken	
	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	101.9	110.6	16.36	6.76	8.09	
	108.5	117.8	16.24	7.25	8.09	
	117.7	127.8	16.32	7.83	8.09	
	110.6	120.1	16.24	7.40	8.09	
	107.2	116.4	16.44	7.08	8.09	
	114.1	123.9	16.47	7.52	8.09	
			n = 6			
			mean	7.31		
			std dev	0.369		0.904
			CV_2	0.0505		
1S	113.6	123.3	16.36	7.54*	17.36	
	268.8	291.9	16.44	17.76	17.36	
	268.8	291.9	16.27	17.94	17.36	
	265.4	288.2	16.33	17.65	17.36	
	259.1	281.3	16.20	17.36	17.36	
	218.3	237.0	16.14	14.68	17.36	
			n = 5			
			mean	17.08		0.984
			std dev	1.357		
			CV_2	0.0794		
2S	550	597	16.41	36.4	35.5	
	490	532	16.20	32.8	35.5	
	509	553	16.30	33.9	35.5	
	565	613	16.26	37.7	35.5	
	543	590	16.42	35.9	35.5	
	440	478	16.44	29.08	35.5	
			n = 6			
			mean	34.3		0.966
			std dev	3.10		
			CV_2	0.0904		
			$\overline{CV}_2$	0.0750		

[Δ]Corrected for DE factor

*This value excluded from statistical analysis based on the Grubb's outlier test as described in Reference 2.

after one day. The data for these samples, given in Table S138-5, show that the samples are stable over a seven-day period; the average recovery was 98.4% for the one-day-old samples vs. 95.2% for the seven-day-old samples.

Migration studies were conducted by analyzing backup sections removed immediately after collection and comparing these to backup sections stored intact for seven days. No n-butylamine was found in any backup section analyzed.

Breakthrough Tests

Breakthrough tests were done in an atmosphere where the relative humidity was 90%. Breakthrough is defined as the time at which the effluent concentration from the collection tube (containing 150 mg of acid-treated silica gel) is 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, when the substance of interest in the test atmosphere is at the 2X OSHA standard level.

The procedures for determining breakthrough in high relative humidity atmospheres together with the description of the equipment used are described in the section on Breakthrough Studies in Attachment B.

When sampling a test atmosphere containing 34.4 mg/cu m at a flow rate of 0.793 liters/min, no breakthrough was observed after 240 minutes, at which time this test was concluded. Under the conditions of this test, the capacity of the sampling tube is at least 6.5 mg or 190 liters.

These tests were conducted at an atmospheric temperature of 22.5° and an atmospheric pressure of 772.3 mm Hg. n-Butylamine has a ceiling standard of 15 mg/cu m, thus limiting the sampling time to fifteen minutes. A maximum sample volume of 15 liters is therefore recommended for n-butylamine. This sample size will yield 0.45 mg of n-butylamine at the 2X OSHA standard level (10 ppm or 30 mg/cu m) at 25°C and 760 mm Hg.

Independent Method of Verifying Generator Concentration

The method used for the independent determination of generator concentration was based on experimentally determining the delivery rate of n-butylamine (in mg/min) into a measured dilution air flow (in cu m/min). On the basis of these two determined values, the Taken generator concentration at the 2S line can be calculated. The concentration at the 0.5S and 1S line can be calculated by measuring the dilution ratio of the 0.5S and 1S line relative to the 2S (main) line.

For the n-butlyamine generation, the syringe delivery rate was calibrated as described in the calibration section in Attachment C; the data

Table S138-5

Data Sheet: n-Butylamine

Storage Stability of Collected Samples

Experiment A: Samples Stored One Day

Test Level	Found				Taken	
	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
1S	113.6	123.3	16.36	7.54*	17.36	
	268.8	291.9	16.44	17.76	17.36	
	268.8	291.9	16.27	17.94	17.36	
	265.4	288.2	16.33	17.65	17.36	
	259.1	281.3	16.20	17.36	17.36	
	218.3	237.0	16.14	14.68	17.36	
			mean	17.08		0.984
			CV_2	0.0794		

Experiment B: Samples Stored Seven Days

1S	224.4	243.6	16.32	14.93	17.36	
	244.0	264.9	16.60	15.96	17.36	
	263.0	285.6	16.11	17.73	17.36	
	241.8	262.5	16.39	16.02	17.36	
	244.0	264.9	16.26	16.29	17.36	
	273.9	297.4	16.35	18.19	17.36	
			mean	16.52		0.952
			CV_2	0.0736		

[Δ] Corrected for DE factor

*This value excluded from statistical analysis based on the Grubb's outlier test as described in Reference 2.

expressed in mg per minute for the replicate determinations are indicated below:

3.817
3.617
3.773
3.887
3.711
3.317

Average = 3.687 mg/min

The corrected main line air flow was determined to be 0.1038 cu m/min at the respective atmospheric temperature and pressure conditions of 24°C and 759 mm of Hg for this generation experiment. In addition, the sample lines were maintained at dilution ratios of 0.228, 0.489 and 1.000 to produce 0.5, 1, and 2X the OSHA standard test levels.

Based on these data, the Taken generator concentrations at the 0.5S, 1S and 2S lines are respectively - 8.09, 17.36 and 35.5 mg/cu m.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S138-3 and S138-4.

Bartlett's test for homogeneity of variances at 0.5, 1 and 2X the OSHA standard for sampling and analysis was applied to the data for n-butylamine. The data (Table S138-4) gave a chi squared value of 1.48, indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation of the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$$\overline{CV}_1 = 0.0490 \qquad \overline{CV}_2 = 0.0750 \qquad \overline{CV}_T = 0.0923$$

The accuracy of the method was determined by comparison of the average value Found by analysis of each set of six samples at each of the three test levels with the Taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 95.1%.

Test Level	-------mg/cu m--------- Taken	Found	Agreement (Found ÷ Taken)
0.5S	8.09	7.31	0.904
1S	17.36	17.08	0.984
2S	35.5	34.3	0.966
		Average -	0.951

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

3. Failure Report on n-Butylamine, No. S138, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

4. LASL Progress Report, Development of Air Monitoring Techniques Using Solid Sorbents, October 1-March 31, 1976, NIOSH Contract 1A-75-31.

5. n-Butylamine, NIOSH Method No. S138, prepared under NIOSH Contract No. 210-76-0123 with validation date July 8, 1977.

ATTACHMENT A

GAS CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the gas chromatography (GC) methods consists of a Varian 2700 Series Gas Chromatograph, a Varian Model 8000 automatic sample injector and a Spectra Physics System 1 computing integrator.

The Varian 2700 is a dual column unit equipped with a flame ionization detector and a photoionization detector (Hnu Systems, Inc.). The unit can be set for isothermal or for linear temperature program operation, either manually or automatically.

The Model 8000 automatic sample injector is mounted horizontally on the Varian 2700 and can readily be moved to align with either of the two injection ports. 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 dry nitrogen, and a control unit which permits total automation in a closed loop form with a computer. For this program, the syringe injector has been set to deliver 5 microliters of sample solution. The unit has been tested to verify that sample to sample cross-contamination does not occur and that the reproducibility of the sample injection is adequate. Periodic checks have been carried out on six or twelve repetitive injections of a standard solution in carbon disulfide and the observed standard deviation of the integrated peak areas is never greater than 2.5%.

All peak area measurements were done with the System 1 computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System 1 also has the capability to calculate sample concentration directly once the calibration factor has been determined.

Approach

The internal standard method (relative area measurements) has been used for this program not only because of its inherently better reproducibility than the external standard method (absolute area measurements) but also as a safeguard against any problems that could arise during the periods of unattended overnight operation. Such problems include detector response variations and the partial clogging of the sample injector loop which can give rise to variability in sample size injections. These clogging effects are caused by the very fine solid sorbent particles which remain suspended in the solution.

A comparative study of the reproducibility of the absolute area and the relative area measurements was performed using sec-butyl acetate (1.5 mg/ml) and undecane as internal standard. The precision of 12 successive determinations was 1.7% based on absolute areas and 0.4% using relative areas.

The choice of an internal standard has been restricted to those compounds which present minimal adsorption losses on the specific solid sorbent used. Experiments have been run to verify adsorption losses by determining the integrated areas of analyte and internal standard in a calibration solution and comparing these areas with the respective areas obtained when 1.0 ml (or other appropriate volume) aliquots of the same calibration solution are added to the appropriate amounts of solid sorbent. (Use the same weight of solid sorbent as that used for sampling.) The ideal internal standard is one which does not show any significant decrease in area due to the solid sorbent addition; this phenomenon is dependent on the interactive characteristics of the internal standard, the solid sorbent and the desorption solvent.

ATTACHMENT B

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S138-B-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 sampling devices are connected in parallel to the 0.5S dilution line and six to the 2S dilution line; twelve sampling devices are connected to the 1S dilution line. All these devices are connected via critical flow orifices (CFO's) to the 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, 0.017 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) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

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

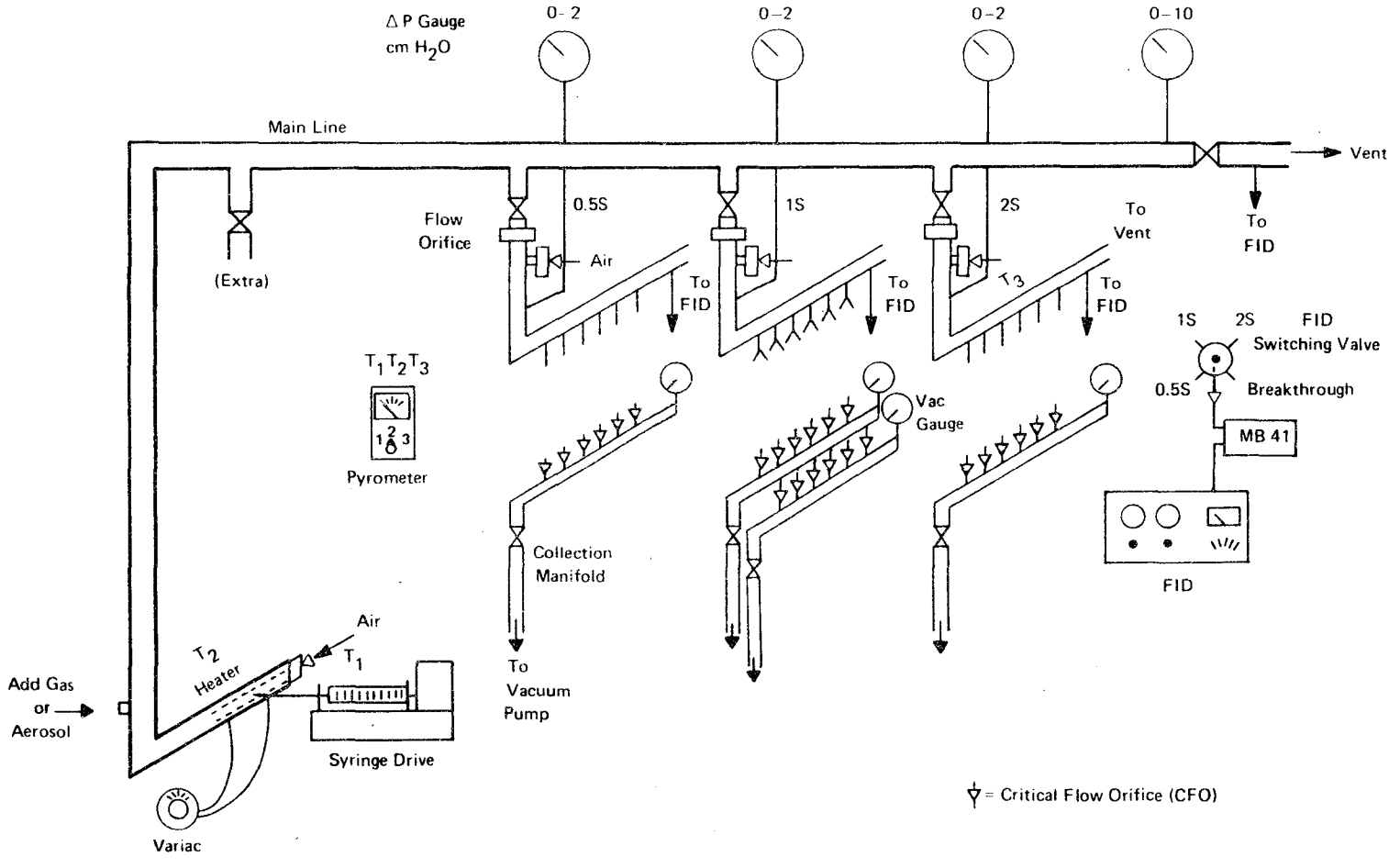


Figure S138-B-1. Vapor Generation/Dilution/Sampling System

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 sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. 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 a 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 (1.5 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

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 0.1086 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.

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	0.499	0.227

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

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. 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. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) 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.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S138-B-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.

2. Sample delivery rate is determined by appropriate calibration.

3. Sample is fed into Main Line until vapor concentration equilibrium is established.

4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.

5. The four sets of six samples from the three concentration levels are collected simultaneously.

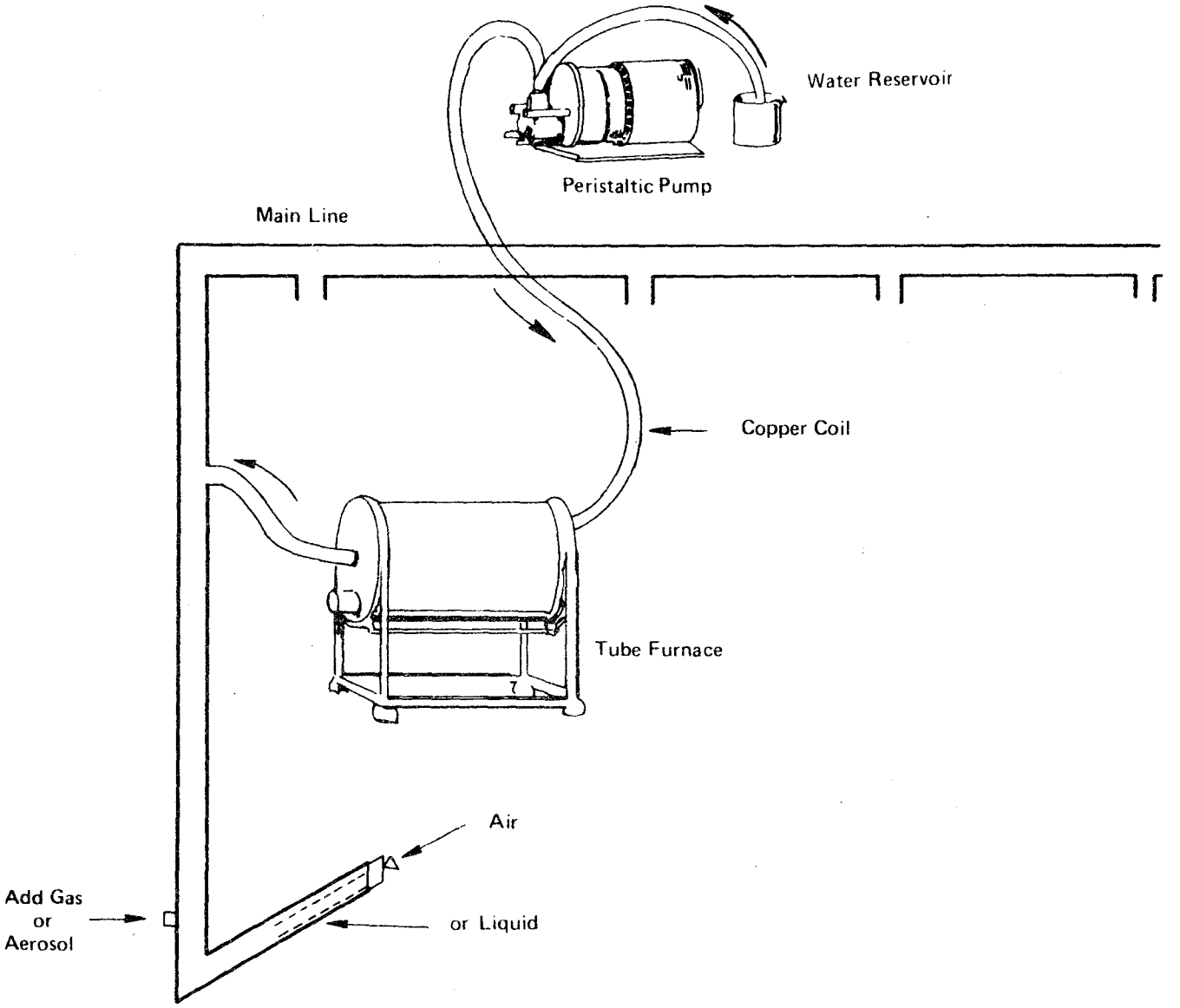


Figure S138-B-2 Generation of High Humidity Atmospheres

ATTACHMENT C

VAPOR GENERATION

Continuous Direct Injection

Vapor concentrations from liquids are generated by adding known amounts of liquid to the Main Line of the vapor dilution/sampling apparatus. A continuous delivery rate is achieved using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25 G stainless steel needle in the Main Line by a short length of 0.16-cm (1/16-in) O.D. Teflon tubing. If the substance of interest is reactive with the stainless steel needle then the Teflon tubing is placed within the Main Line replacing the needle. When dealing with liquids of low volatility the 25G needle is mounted such that the tip of the needle rests inside a 10-cm length of 8-mm I.D. 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.

Calibration of Syringe Delivery

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 25-800 mg are collected depending on the specific compound being studied.

Calculation of Main Line 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.

2-Aminopyridine

Analyte:	2-Aminopyridine	Method No.:	S158
Matrix:	Air	Range:	0.91-3.60 mg/cu m
OSHA Standard:	0.5 ppm (2 mg/cu m)	Precision ($\overline{CV}_T$):	0.061
Procedure:	Adsorption on Tenax GC, thermal desorption, GC	Validation Date:	9/30/77

1. Principle of the Method

1.1 A known volume of air is drawn through two glass tubes in series containing Tenax GC to trap 2-aminopyridine vapors.

1.2 2-Aminopyridine is thermally desorbed from the Tenax GC, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.913-3.59 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 758 mm Hg, using a 12-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method depends on the adsorptive capacity of the Tenax GC. This capapcity may vary with the concentrations of 2-aminopyridine and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 35 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of 0.184 liter/minute and relative humidity of 84% and temperature of 25°C. The breakthrough test was conducted at a concentration of 4.10 mg/cu m.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as 2-aminopyridine at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.913-3.59 mg/cu m was 0.061. This value corresponds to a 0.12 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.4% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.56 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of 2-aminopyridine found on the backup Tenax GC tube exceeds 25% of that found on the front tube, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

6.2 Tenax GC Tubes: Separate front and backup sampling tubes are used in this method. The tubes are constructed of glass tubing with both ends unsealed. The tubes are 13 cm long with a 6-mm O.D. and a 4-mm I.D. The front tube contains 35 mg of 35/60 mesh Tenax GC*, and the

* Tenax GC is a solid adsorbent manufactured by Enka, N.V., The Netherlands. It is available through most gas chromatographic equipment suppliers.

backup tube contains 17 mg. Tenax GC is held in place in the tube with 3-mm plugs of glass wool. The Tenax GC is placed within 4 cm of one end of the tube. The sample tube length may need to be adjusted to accommodate the GC inlet. The pressure drop across the tubes must be less than 10 mm of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Before use, each tube must be thermally desorbed for 3 minutes at 240°C using a nitrogen flow through the tube to rid the Tenax GC of any interfering substances. The front and backup tubes are joined together with a short piece of flexible tubing, and the ends of the sampling train are capped with plastic caps.

6.3 Thermal Desorption Apparatus: This apparatus is designed to use the gas chromatograph inlet heater as the source of heat for thermal desorption. The inlet should have an opening of at least 6 mm in diameter and be deep enough to allow the sample tube to be inserted. The apparatus consists of three parts as illustrated in Figures S158-1 and S158-2.

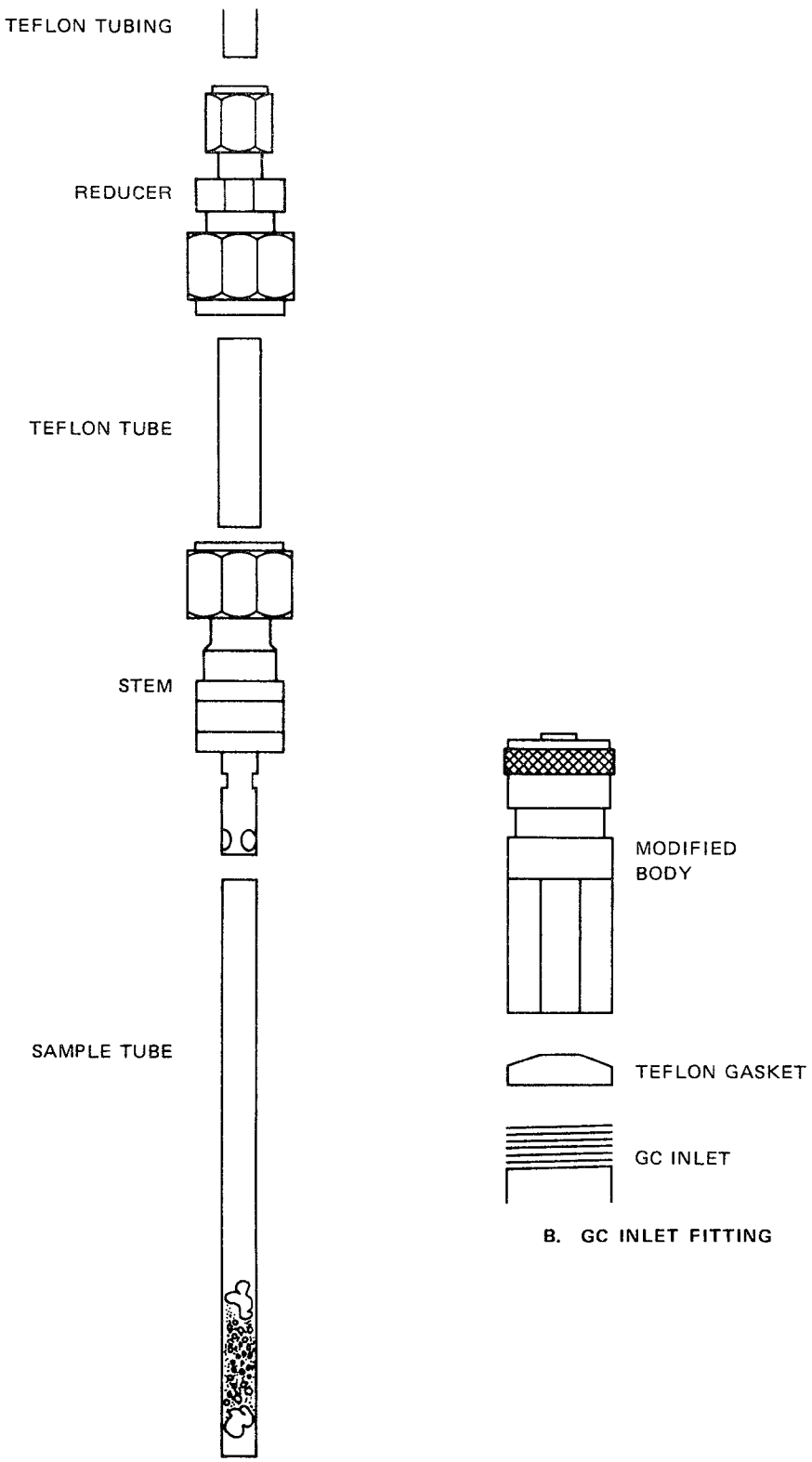
6.3.1 Sample Tube Holder (Figure S158-1A): This assembly is composed of a Swagelok Quick-Connect** stem (stainless steel #QC6-S-600) with a 3/8-in tube fitting on the opposite end. The fitting is drilled out to allow the 6-mm O.D. sample tube to pass through it. A Teflon tube (4 cm long with a 3/8-in O.D. and 5.5 mm I.D.) connects the stem to a 3/8 in to 1/4 in tube fitting reducer. Teflon ferrules are used with the connecting nuts to hold the Teflon tube. The sample tube is inserted through the stem and into the Teflon tube. Tightening the connecting nut to finger tightness secures the sample tube in place. The Teflon tube may have to be replaced after excessive use.

6.3.2 Gas Chromatograph Inlet Fitting (Figure S158-1B): This assembly consists of a Swagelok Quick-Connect** body (stainless steel #QC6-B-4PF) which has been rethreaded to fit onto the gas chromatograph injection port. The ball and spring in the body must be removed to allow the sample tube to pass through. This fitting replaces the septum nut. Other injector parts that interfere with insertion of the sample tube must be removed.

The inlet fitting is sealed to the injection port with a Teflon gasket.

6.3.3 Valves and Carrier Gas Lines (Figure S158-2): The flow of carrier gas is regulated by a system incorporating two needle valves and two 3-way valves. The carrier gas is split into two lines regulated by needle valves. When a sample tube is being thermally desorbed, the majority of carrier gas flows

**Patented by Crawford Fitting Company.



A. SAMPLE TUBE HOLDER

B. GC INLET FITTING

FIGURE S158-1

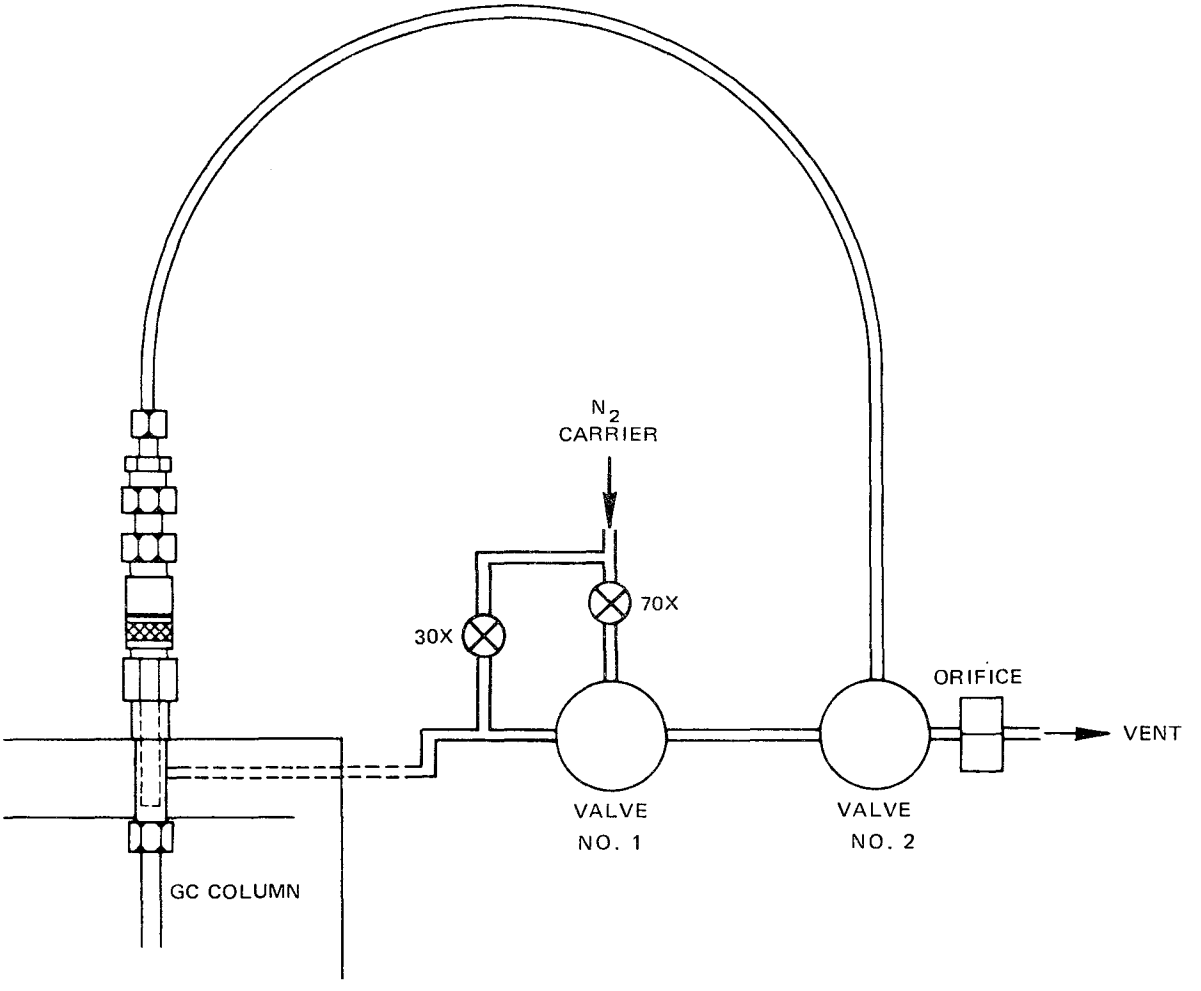


FIGURE S158-2 VALVES AND CARRIER GAS LINES

through the sample tube. A minor flow enters at the normal GC inlet port to allow additional carrier gas to flow over the sample tube. Three-way valve #1 is used to split the carrier flow as described above or route the entire flow to the inlet port for normal use of the GC or injection of standards. Three-way valve #2 is used to vent the carrier flow when the sample tube holder is being loaded with a sample tube. It is also used to relieve pressure before disconnecting the desorber from the inlet after a sample is analyzed. A 0.02-in flow limiting orifice is placed at the valve #2 vent so that pressure is relieved slowly. Sudden changes in pressure may disrupt the gas chromatographic column packing or the sorbent in the sample tube. The thermal desorption assembly is connected to valve #2 with a 1/4-in O.D. Teflon tubing.

6.4 Gas Chromatograph equipped with a flame ionization detector.

6.5 Column (5-ft long x 1/4-in O.D. glass) packed with Carbopack B coated with 4% Carbowax 20M and 0.8% KOH.

6.6 An electronic integrator or some other suitable method of determining peak areas.

6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.

6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.

6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.

6.10 Stopwatch.

6.11 Manometer.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 2-Aminopyridine, reagent grade.

7.2 Nitrogen, purified.

7.3 Hydrogen, prepurified.

7.4 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative Tenax GC tubes in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tubes. All tubes must be packed with Tenax GC from the same manufacturer's lot.

8.3.2 The tube containing the smaller amount of Tenax GC is used as a backup tube and should be positioned nearer the sampling pump. Air should flow through the front tube before entering the backup tube.

8.3.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tubes.

8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record sampling time, flow rate, and type of sampling pump used.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The Tenax GC tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Tenax GC tube with its corresponding backup tube.

8.3.8 With each batch of 10 samples, submit one set of tubes (a front adsorbing tube containing 35 mg of Tenax GC and a backup tube containing 17 mg of Tenax GC) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Tenax GC tubes. A minimum of 18 extra Tenax GC front and backup tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the caps from the ends of the sample tube. Wipe off the outside of the tube with a clean lab wiper.

8.4.2 Thermal Desorption of Samples

1. Place auxillary valves in position so that the carrier gas is split between the sample tube holder and the inlet (valve #1 dividing flow) and so that flow to the sample tube holder is vented (valve #2 open to vent).

2. Load the sample tube holder by inserting the sample tube through the stem and just into the Teflon tube with the connecting nut loose. Tighten the connecting nut to finger tightness to secure the sample tube in place. The sorbent material should be at the end opposite the connecting nut.

3. Insert the sample tube into the gas chromatograph inlet, joining the stem of the sample tube holder to the body of the gas chromatograph inlet fitting.

4. Turn the carrier gas valve #1 to allow the carrier gas to pass through the sample tube.

5. Allow the sample to thermally desorb for 3 minutes at an inlet temperature of 240°C onto the head of the GC column which is set at 125°C.

6. Program the column oven temperature from 125°C to 225°C at a rate of 25°C/minute.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. Thermal desorption mode - 60 ml/min nitrogen carrier gas flow through sample tube holder; 20 ml/min nitrogen carrier gas flow to inlet.

2. Standards injection mode - 80 ml/min nitrogen carrier gas flow to inlet.

3. Both modes - 50 ml/min hydrogen gas flow to detector; 500 ml/min (50 psig) air flow to detector.

8.4.4 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Tenax GC.

8.5.2 Tenax GC sample tubes containing 35 mg of Tenax GC from the same batch as that used in obtaining the samples are used to determine the desorption efficiency. A known amount of a water solution of 2-aminopyridine is injected directly onto the Tenax GC with a microliter syringe, and the tube is capped. The amount injected is equivalent to that present in a 12-liter air sample at the selected level. The solutions of 2-aminopyridine in water are prepared so that the amount injected is no more than 2.0 microliters. This is to minimize the effects of excess solvent on the GC column.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared and allowed to stand for at least overnight to assure complete adsorption of the 2-aminopyridine onto the Tenax GC. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are thermally desorbed and analyzed in exactly the same manner as the sampling tubes described in Section 8.4.

To inject standards into the GC, the normal septum injection port is installed and all of the carrier gas is allowed to flow through the normal inlet position (valve #1 combining flow). The same volume of 2-aminopyridine is injected directly into the GC injection port with the same syringe used in preparation of the samples.

To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. One microliter of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from

the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. No more than a 3% difference in area is to be expected between duplicate injections.

Standards are injected into the GC with column oven temperature set at 125°C.

Immediately after injection, the oven temperature is programmed to 225°C at a rate of 25°C/minute. Standards are analyzed before and after a set of samples is analyzed.

The desorption efficiency (D.E.) equals the average weight in µg recovered from the tube divided by the weight in µg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (µg)}}{\text{Weight added (µg)}}$$

The desorption efficiency is dependent on the amount of 2-aminopyridine collected on the Tenax GC. Plot the desorption efficiency versus weight of 2-aminopyridine found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms versus peak area. Standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

9.1 Prepare a stock standard solution containing 345 mg/ml of 2-aminopyridine in water.

9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in water. Prepare at least 5 working standards to cover the range of 2.3-70 micrograms/sample. This range is based on a 12-liter sample and 2-microliter injections.

9.3 Prepare a standard calibration curve by plotting micrograms 2-aminopyridine versus peak area.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in front sample tube
µg blank = µg found in front blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{DE}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2}} \times \frac{T_2}{T_1} \right)$$

where:

f = flow rate sampled
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.6 The concentration of 2-aminopyridine in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \mu g/\text{liter} = \frac{\text{Corrected } \mu g \text{ (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of 2-aminopyridine = 94.1
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication # 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-03-00231-2.

11.2 Backup Data Report for 2-Aminopyridine, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S158

September 30, 1977

Substance

2-Aminopyridine

Standard

8-hour time-weighted average: 0.5 ppm (2.0 mg/cu m)

Analytical Method

A known volume of air is drawn through two tubes in series each containing 35/60 mesh Tenax GC to trap the 2-aminopyridine vapors present. The 2-aminopyridine is thermally desorbed from the Tenax GC and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 0.913-3.59 mg/cu m for a 12-liter sample at 24°C and 758 mm Hg atmospheric temperature and pressure.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow can be determined accurately (±5%) in the range of 0.01 to 0.2 liter per minute. Two tubes (each tube is 13 cm long with a 6-mm O.D. and 4-mm I.D.) connected in series are used to collect the samples. The front tube contains 35 mg of Tenax GC, and the backup tube contains 17 mg. The Tenax GC is held in place in the sample tube with 3-mm plugs of glass wool. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Before use of the tubes, each Tenax GC tube must be thermally desorbed for 3 minutes at 240°C with nitrogen to rid the Tenax GC of any interfering substances.

Sample Size

A sample size of 12 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter/minute. Do not sample at a flow rate less than 0.01 liter/minute.

Sampling Procedure

1. Immediately before sampling, remove the caps from the ends of the tube. All tubes must contain Tenax GC from the same manufacturer's lot.

2. The tube containing the smaller amount of Tenax GC is used as a backup and should be positioned nearer the sampling pump. The two tubes are connected with a small piece of flexible tubing. Air should flow through the front tube before entering the backup tube. The tubes should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of 2-aminopyridine.

3. Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tube.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature, relative humidity, and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump that is used.

5. The Tenax GC tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Tenax GC tube with its corresponding backup tube.

6. With each batch of ten samples, submit one set of tubes (a front adsorbing tube containing 35 mg of Tenax GC and a backup tube containing 17 mg of Tenax GC) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

Special Considerations

1. When other compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

2. Due to the high resistance of the Tenax GC tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without first fully recharging the battery.

3. The volume recommended is based on high humidity breakthrough tests. Further reduction in sample volume due to high humidity should not be needed. If condensation of water occurs in the tube, the substance may not be trapped quantitatively.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Capped Tenax GC tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tube.

Reference

2-Aminopyridine, NIOSH Method No. S158.

Backup Data Report No. S158

September 30, 1977

Substance: 2-Aminopyridine

OSHA Standard: 0.5 ppm (2 mg/cu m)

Chemical Used for Validation: 2-Aminopyridine, 99+% Gold Label Aldrich Chemical Company

General

The procedure for collection and analysis of air samples of 2-aminopyridine is described in NIOSH Method No. S158. This method consists of collection of the sample on Tenax GC, thermal desorption, and analysis by gas chromatography.

This method has been tested for validity for a 12-liter air sample using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at the OSHA standard level 95% of the time.

The protocol used for testing this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of 2-aminopyridine to represent 12-liter air samples.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

Determine the breakthrough capacity of Tenax GC at high relative humidity.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S158. The results of the desorption efficiency tests are in Table S158-5. Tenax GC, Lot 4901, was used in the validation study.

Sampling and Analysis

Test atmospheres of 2-aminopyridine in air were generated with the vapor generation apparatus described in Attachment A. Solid crystalline 2-aminopyridine was placed in the vapor generator. The generator was immersed in a constant temperature water bath and a flow of air passed through the 2-aminopyridine. The amount of vapor generated is dependent upon the vapor pressure of the material, the bath temperature, and the flow of air. The required levels of 2-aminopyridine were generated at a water bath temperature of 22.5°C and an air flow rate of 0.6 liter/minute. Dilution air was added downstream to obtain samples at 2X, 1X, and 0.5X the OSHA standard. An all glass dilution system and sampling manifold was used, because nonreproducible results were obtained when 2-aminopyridine was collected from a stainless steel system. Surface reactions may have been the cause of losses and nonreproducibility of generated atmospheres in the stainless steel system. The glass dilution system is described in Attachment A. The samples were collected using two tubes connected in series each containing Tenax GC. The first tube contained 35 mg of Tenax GC, and the second tube contained 17 mg.

Six samples were collected for 4000 seconds at each level to obtain 12-liter air samples. An additional six samples were collected at 1X the OSHA standard level and were used for the storage stability test. The results of the analysis of these samples are in Table S158-6. In addition, the backup sections of the sampling tubes at the 2X level were analyzed and found to contain less than the limit of detection, which was 0.3 microgram.

Storage Stability Study

A study was done to assess whether 2-aminopyridine would be successfully stored for one week after collection. A second set of six samples at 1X the OSHA standard level was collected at the same time as the samples that were used for validation. Samples were collected as described under the Sampling and Analysis section. Samples were collected for 4000 seconds at an average flow rate of 0.18 liter/minute. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results of the analyses are presented in Table S158-1.

Table S158-1

Storage Stability

Samples Analyzed Immediately (mg/cu m)	Samples Analyzed After One Week (mg/cu m)
1.485	1.435
1.471	1.393
1.483	1.389
1.407	1.374
1.529	1.453
1.578	
mean 1.492	1.409
std dev 0.058	0.034
CV 0.039	0.025

The criterion for acceptance was that the mean of the samples stored at room temperature for seven days should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 6%; thus, storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed at a relative humidity of 84%. Details of the method of generating atmospheres containing high relative humidities are given in Attachment B.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 35 mg of Tenax GC) 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, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

Since the concentration of 2-aminopyridine in the air samples was too low to monitor directly, it was necessary to measure the amount collected on the front and backup tubes and calculate the breakthrough time.

The breakthrough time was measured by testing 13 sample tubes in parallel; each of the sample tubes containing 35 mg of Tenax GC. Each sample tube was followed by a backup tube containing 17 mg of Tenax GC. The tubes were placed in the sample generation apparatus. The test atmosphere was caused to flow through each pair of tubes at the flow rate to be used during sample collection. After start of the test, a sample tube and corresponding backup tube was analyzed at 30 minutes and every 15 minutes thereafter. The amount of 2-aminopyridine collected on the sample and backup tubes was determined by thermal desorption of

the sample with subsequent GC analysis.

The test chamber was also sampled independently by collecting sequential samples with a bubbler containing deionized water. Determinations were made by uv absorption. The data collected during the breakthrough test are presented in Table S158-2.

Table S158-2
Breakthrough Test

Time (hours)	µg Found (front)	µg Found (backup)
0.50	19	N.D.*
0.75	33	N.D.
1.00	44	N.D.
1.25	54	N.D.
1.50	65	N.D.
1.75	78	N.D.
2.00	68	N.D.
2.25	96	N.D.
2.50	106	N.D.
2.75	129	N.D.
3.00	156	N.D.
3.25	183	N.D.
3.50	203	N.D.

* N.D. = Not detected at a detection limit of 0.3 microgram.

Breakthrough did not occur when the average sampling rate was 0.184 liter/minute when the relative humidity was 84%. The concentration tested was 4.10 mg/cu m. Sampling was discontinued after 210 minutes. The breakthrough test was discontinued, because of a limited number of sampling ports.

Discussion

Previous experimental work (Reference 3) on 2-aminopyridine was based upon collection of the analyte in a bubbler containing 0.05 M sulfuric acid and analysis of the collected samples by gas chromatography of an aliquot of the sample after making it alkaline. A precolumn was required to absorb salts and protect the GC column. The GC column required special treatment to remain functional. Because of the difficulties encountered, a different approach of collection and analysis was attempted.

The selection of the present method was based upon several considerations. A solid sorbent such as Tenax GC is a very desirable collecting medium in field sampling. It has a high capacity and remains effective

under humid conditions. Thermal desorption of the sample was appropriate since no solvents are required. In GC analysis of amines, solvents have caused GC column breakdown and reproducibility problems. In addition, thermal desorption increases sensitivity since the entire sample is analyzed. As a result, analysis by gas chromatography is simplified.

A breakthrough test was initially run using sample tubes containing 18 mg of Tenax GC, at a sampling flow rate of 0.5 liter/minute. Breakthrough occurred in 45-60 minutes. The test atmosphere was generated at 84% relative humidity and concentration of 4.1 mg/cu m.

A preliminary storage stability study was run on Tenax GC sample tubes which were spiked with standard solutions of 2-aminopyridine. The sample tubes were capped and stored on the laboratory bench for 42 days before analysis. The results are presented in Table S158-3.

Table S158-3

Storage Stability, Spiked Samples

µg taken	µg found		Recovery
24.00	22.96		0.957
24.00	22.87		0.953
24.00	21.32		0.888
24.00	22.55		0.940
24.00	20.48		0.853
		mean	0.918
		std dev	0.046
		CV	0.050

Independent Method

To determine the concentration of 2-aminopyridine in the test atmosphere, samples were collected in midget bubblers containing deionized water, and the absorbance of the samples was read at 290 nm. A standard curve was prepared over the range of 0-26 micrograms/ml 2-aminopyridine in water. This produced a linear curve from 0 to 1.0 absorbance units.

The results of samples collected from the generated test atmosphere are presented in Table S158-4. Samples at the 2X level were taken in two sets, each set taken over half the sampling period. Samples at the 1X and 0.5X level were taken over the entire sampling period.

Table S158-4

Independent Method

Level		mg/cu m	
2X		3.70	1st half
		3.62	
		3.63	
		3.59	2nd half
		3.39	
		3.63	
	mean	3.59	
	std dev	0.11	
	CV	0.031	
1X		1.600	
		1.500	
		1.590	
	mean	1.560	
	std dev	0.055	
	CV	0.035	
0.5X		0.941	
		0.922	
		0.877	
	mean	0.913	
	std dev	0.033	
	CV	0.036	

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2.

The precision of the analytcial method was assessed using the data in Table S158-5. The pooled Coefficient of Variation ($\overline{CV_1}$) for three sets of analytical samples was found to be 0.038.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S158-6 and the results obtained from breakthrough tests and storage stability tests. The pooled Coefficient of Variation (CV_2) for the three sets of samples collected from test atmospheres is 0.032. To obtain a measure of the accuracy of the method, the mean value of the concentration found by analysis at each level was compared with the value for the concentration taken.

The average recovery (concentration found divided by concentration taken) for all three levels was 98.6%. The value for the taken concentration was obtained as described under the Independent Method Section. The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test described above.

The total Coefficient of Variation ($\overline{CV}_T$) is 0.061.

Table S158-5

Data Sheet: 2-Aminopyridine

Analysis

Level	0.5X			1X			2X	
µg taken	µg found	DE	µg taken	µg found	DE	µg taken	µg found	DE
11.45	11.73	1.024	22.90	23.36	1.020	41.9	45.3	1.081
11.45	10.01	0.874	22.90	22.25	0.972	41.9	43.8	1.045
11.45	11.54	1.008	22.90	22.98	1.004	41.9	43.1	1.029
11.45	11.00	0.961	22.90	23.10	1.009	41.9	45.3	1.081
11.45	10.99	0.960	22.90	21.70	0.948	41.9	43.4	1.036
11.45	11.07	0.967	22.90	21.95	0.959	41.9	44.1	1.052
n=		6			6			6
mean		0.966			0.985			1.054
std dev		0.052			0.030			0.022
CV_1		0.054			0.030			0.021

$\overline{CV}_1$ 0.038

$\overline{CV}_{A+\overline{DE}}$ 0.041

Table S158-6

Data Sheet: 2-Aminopyridine

Sampling and Analysis

Test Level	Found			Taken	Percent Recovery
	µg	Liters	mg/cu m*	mg/cu m	
0.5X	10.29	11.60	0.887	0.913	
	12.10	13.07	0.926	0.913	
	10.47	11.93	0.878	0.913	
	10.22	11.07	0.923	0.913	
	11.67	12.33	0.946	0.913	
	11.21	12.20	0.919	0.913	
		n = 6			
		mean	0.913		100.0
		std dev	0.026		
		CV_2	0.028		
1X	17.52	11.80	1.485	1.560	
	16.78	11.41	1.471	1.560	
	17.22	11.61	1.483	1.560	
	17.33	12.32	1.407	1.560	
	18.75	12.26	1.529	1.560	
	19.03	12.06	1.578	1.560	
		n = 6			
		mean	1.492		95.6
		std dev	0.058		
		CV_2	0.039		
2X	41.6	12.00	3.47	3.59	
	40.2	11.47	3.50	3.59	
	48.2	13.13	3.67	3.59	
	44.3	11.87	3.73	3.59	
	40.4	11.00	3.67	3.59	
	44.3	12.33	3.59	3.59	
		n = 6			
		mean	3.60		100.3
		std dev	0.10		
$\overline{CV_2}$ 0.032		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. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-03-00231-2.

3. 2-Aminopyridine Failure Report, No. S158, prepared under NIOSH Contract CDC-99-74-45.

Attachment A

Vapor Generation System

Test atmospheres of organic vapors can be generated with an apparatus described in Reference No. 1, which describes a method for measuring liquid vapor pressure.

The vapor generator was adapted from the apparatus described in Reference No. 1. A schematic diagram of this vapor generator is shown in Figures S158-A1 and S158-A2. The vapor generator consists of two sections--a generating section (Figure S158-A1) and a diluting section (Figure S158-A2) which are connected by a ground glass joint.

The generating section (Figure S158-A1) 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, low melting solid, or a solid with a high vapor pressure, 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. Air is introduced through the small tube and passes through the frit. The small bubbles, which form at the frit, rise through the liquid or solid and become saturated or nearly saturated with the vapor. The bath temperature and the flow of air determine the actual amount of vapor generated. Increasing either the air flow or the bath temperature, increases the amount of vapor generated.

The diluting section (Figure S158-A2) 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 air to the desired concentration. Vapor saturation of the air stream must not be exceeded.*

Dilution air and the vapor in air are mixed in two 9/16-in I.D. x 18-in long sections of glass tubing constructed with internal baffles. The diluted vapor flows into a 2-liter glass sphere which has 15 glass sampling ports. Excess vapor passes through the glass sphere to a fume hood.

The equations given in Reference No. 1 can be used to determine the approximate vapor concentration in the saturated nitrogen stream.

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1. Physical Methods of Chemistry, Part V, A.Weissberger and B. W. Rossiter, eds., (John Wiley & Sons, 1971), 61-66.

*If the vapor saturation concentration is exceeded, particles will be formed in the cool air stream.

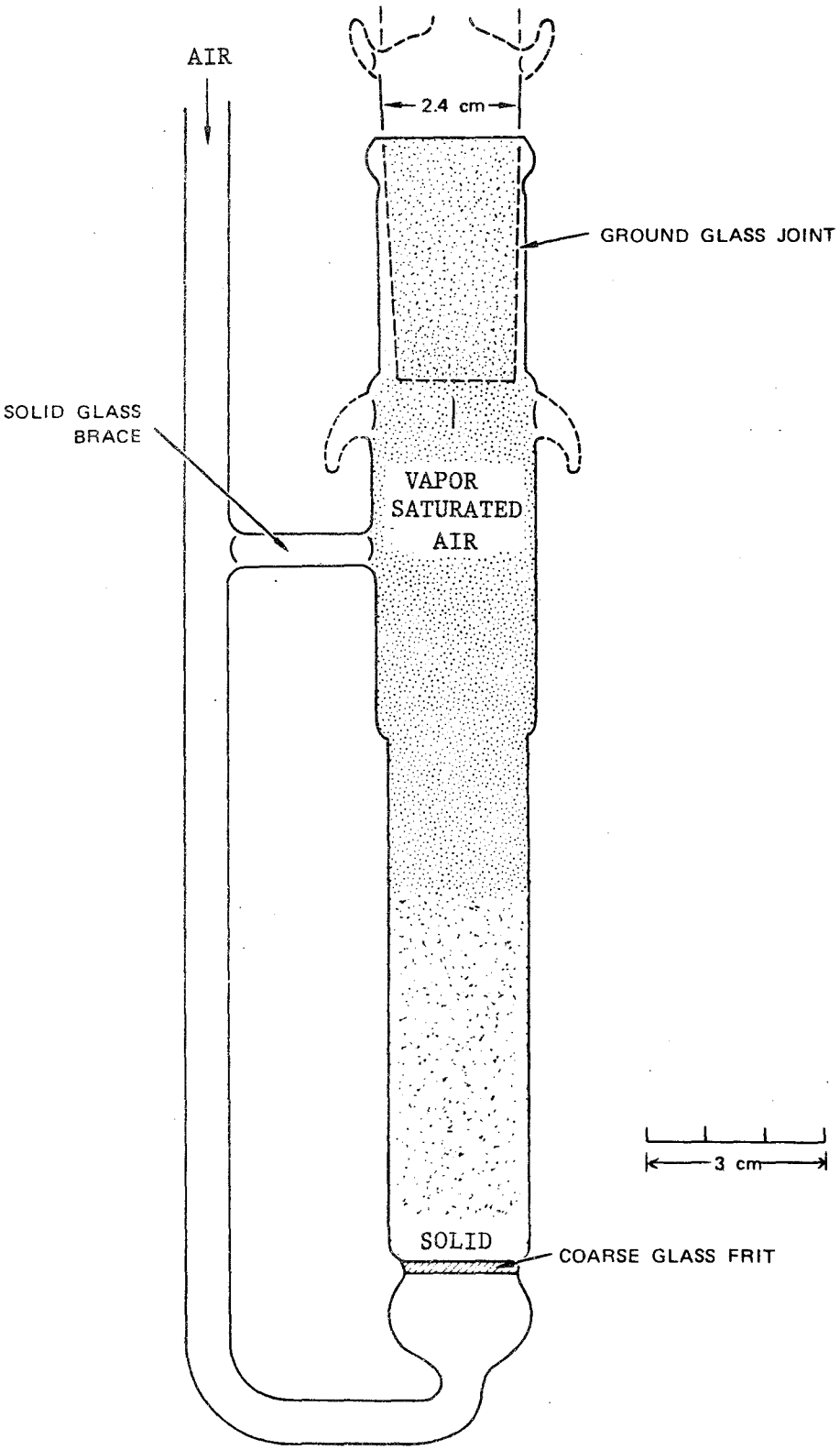


FIGURE S158-A1 VAPOR GENERATOR (generating section)

87<

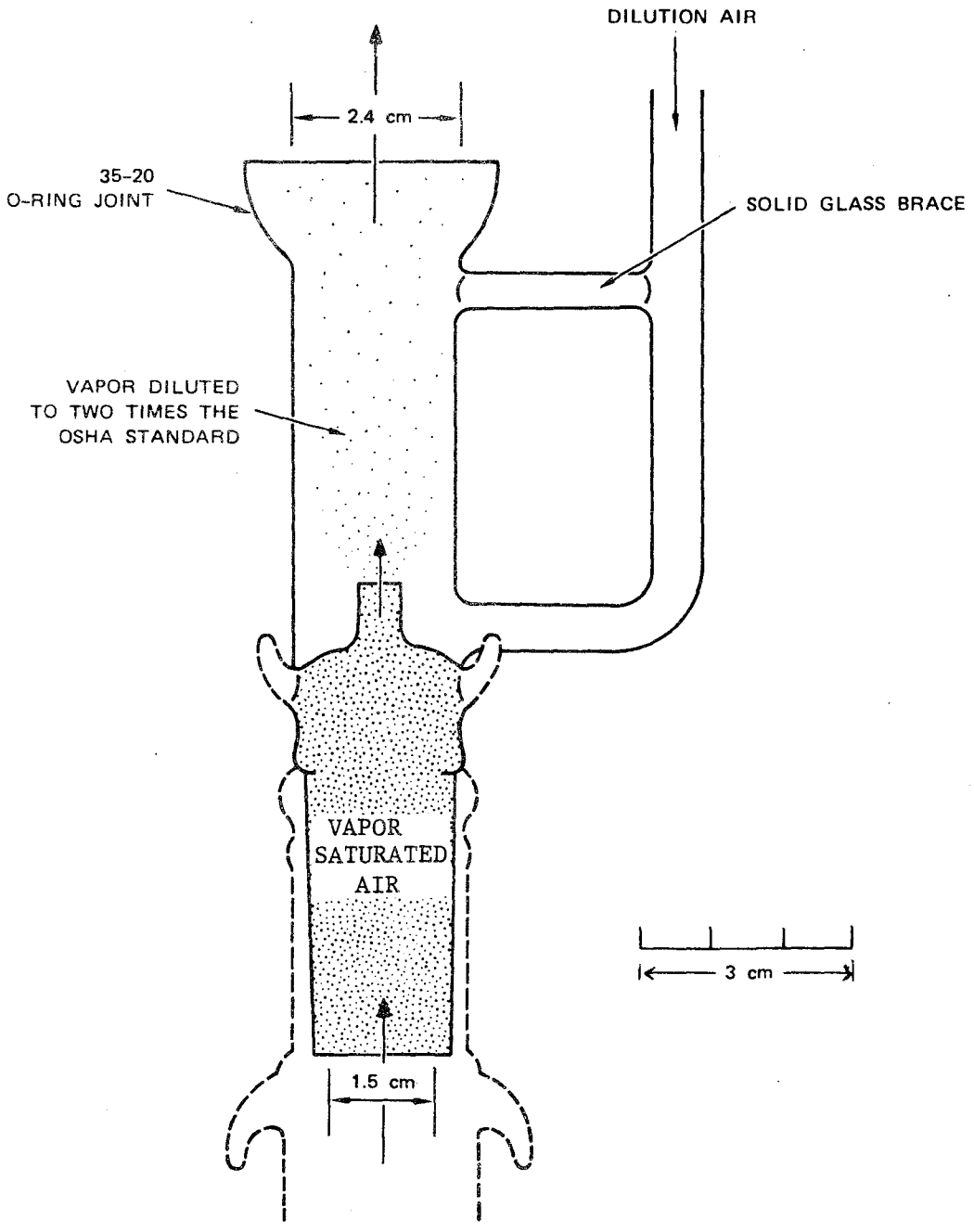
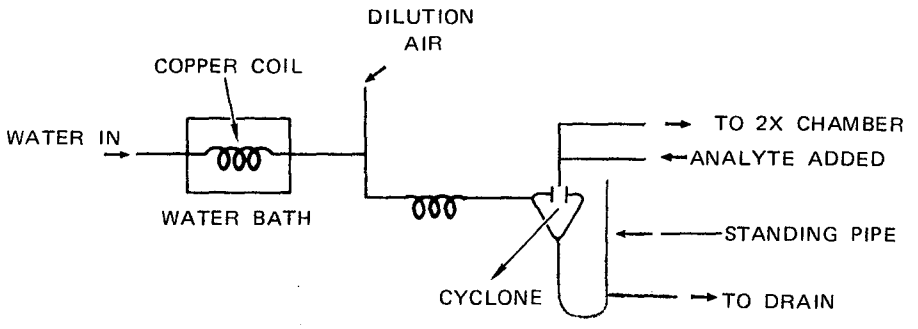


FIGURE S158-A2 VAPOR GENERATOR (diluting section)

Attachment B

Generation of Known Humidity Test Atmospheres

A diagram of the apparatus used for generating high humidity atmospheres is shown below.



A regulated flow of tap water at approximately 15°C flows through a copper coil contained in a thermostated water bath. After emerging from the water bath it enters a 5-foot length of 5/16-inch Tygon tubing. The dilution air is introduced into this same tubing and becomes water saturated at the temperature of the bath. This water-air mixture passes into a cyclone, where excess water is removed from the air stream and drains from the bottom of the cyclone. The U-shaped tube and standing pipe provide a water seal at the bottom of the cyclone to prevent loss of air by this route. The humid air passes through the top of the cyclone. A controlled flow of the analyte enters the air stream at the outlet of the cyclone at a rate such that the 2X concentration is obtained.

The temperature of the water bath is kept 1°C lower than the temperature of the room. Thus, the air is saturated with water vapor at the lower temperature and reaches a relative humidity of less than 100% as it warms to room temperature after leaving the cyclone.

The relative humidity of the air in the sampling chamber is measured by the dry and wet bulb thermometer method. A flow of 32 liters/minute of the test atmosphere is drawn from the sampling chamber over the thermometers.

To ensure that a sufficiently high flow rate of air passes over the thermometers to give an accurate measurement, both thermometers are enclosed in glass tubing with an internal diameter of 11 mm.

From the readings of the relative temperatures of these two thermometers, the relative humidity at the temperature of the dry thermometer is found by consulting relative humidity tables.

Quinone

Analyte:	Quinone	Method No:	S181
Matrix	Air	Range:	0.17-0.75 mg/cu m
OSHA Standard:	0.4 mg/cu m	Precision ($\overline{CV}_T$):	0.085
Procedure:	Adsorption on XAD-2, desorption with ethanol/hexane, analysis by HPLC	Validation Date:	9/30/77

1. Principle of the Method

1.1 A know volume of air is drawn through a tube containing XAD-2 resin to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

1.2 The XAD-2 in each tube is transferred to a vial and the quinone is desorbed with a solution of 20% ethanol in hexane and analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.17-0.75 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 767 mm Hg using a 24-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at 81% relative humidity when sampling a test atmosphere at 2 times the OSHA standard. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The detection limit of this method is estimated to be at most 0.4 nanograms of quinone based on an injection volume of 20 µl.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, solvent composition, etc.) must be changed to solve the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.17-0.75 mg/cu m was 0.0847. This value corresponds to a 0.0339 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentrations "found" at the OSHA standard level using the overall sampling and analytical method were 1.1% higher than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.2). Any difference between the two concentrations does not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 All samples must be analyzed within one hour of desorption and interspersed among standard solutions prepared within an hour. This limits the number of samples which can be analyzed at once, but is necessary since the solutions are unstable and may not give reliable results after an hour.

5.3 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of micrograms that the tube will hold before overloading. When an atmosphere at 81% relative humidity containing 0.794 mg/cu m of quinone was sampled at 0.2 liter per minute, 1.6% breakthrough was observed after 240 minutes (capacity is at least 45 liters or 37 µg). The sample size recommended is less than the 5% breakthrough capacity at 81% R.H. for a test atmosphere at 2 times the OSHA standard to minimize the probability of overloading the sampling tube.

5.4 When the sample value obtained for the backup section of the sorbent tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.5 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Apparatus

6.1.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.1.2 Sampling Tube. Glass tube with both ends flame-sealed, 10-cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.2 High pressure liquid chromatograph. The unit must be capable of UV detection at 240 nm.

6.3 Column, 25-cm x 4.6-mm I.D. x 1/4" stainless steel Partisil^{tm} PXS 10/25 ODS or equivalent.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Twelve-milliliter screw cap vials with Teflon-lined caps.

6.6 Microliter syringes, 10, 25, 50, 100 and 250-microliter and other convenient sizes for preparing standards.

6.7 Pipet, 5-ml, delivery type.

6.8 Volumetric flasks, 25-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Ethanol, absolute.

7.2 Hexane, chromatographic quality, distilled in glass.

7.3 Quinone, reagent grade.

7.4 Twenty percent ethanol in hexane. Prepare by diluting 200 ml of absolute ethanol to 1000 ml with hexane. This solvent is used for making standard solutions and as a desorption solvent. It is also the mobile phase for the HPLC analysis and is degassed for such use.

7.5 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Larger batches may be prepared by using a large size Soxhlet extractor. Overnight (24 hours) extractions are then performed successively with water, methanol, diethylether and n-pentane. Finally, several washings with 20% ethanol in hexane are recommended to reduce possible interferences to a minimum when the sorbent is desorbed with this solvent. Distilled-in-glass solvents are used in all cases. Resin has been prepared in this manner using charges of about 700 grams of resin and 1.5 liters of each solvent. The resin is dried in a fluidized bed process using nitrogen gas at room temperature from a liquid nitrogen cylinder. The drying process is terminated when no organics are detected experimentally in the effluent. A final quality control check is performed by desorbing a portion of the resin and analyzing the resulting solution by gas chromatography. Residual organics should be less than 1000 ppm in concentration.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sampling tube series in the line; the tube is described in Section 6.1.2. This will minimize the errors associated with uncertainities in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (2-mm).

8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The resin tube series chould be placed in a vertical direction during sampling to minimize channeling through the resin.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the resin tube.

8.3.5 A sample size of 24 liters is recommended. Sample at a known flow rate between 0.2 and 0.01 liter per minute for 120 minutes. The flow rate should be known with an accuracy of at least ± 5%.

8.3.6 Record the ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 The resin tube should be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 With each batch of 10 samples, submit one resin tube which has been handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped resin tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 Arrange to have samples analyzed within seven days.

8.3.11 Minimize exposure to light and refrigerate samples.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the front 100-mg section is transferred to a 12-ml vial. The separating section of glass wool is removed and discarded. The second 50-mg section is transferred to another vial. These two sections are analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis 5.0 ml of 20% ethanol in hexane is pipetted into each 12-ml vial. The vial is capped immediately after solvent addition and then agitated. Since all samples must be analyzed within an hour of desorption it is extremely important to desorb only as many samples as can be analyzed within that period of time. The number of standards to be analyzed simultaneously must be taken into account as well. All samples may be analyzed as soon as desorbed. Tests have shown this is

a sufficient time for desorption provided the samples are shaken after solvent addition.

8.4.3 HPLC Conditions. The mobile phase is 20% ethanol in hexane. Typical operating conditions for the chromatograph are:

1. 2 ml/min solvent flow
2. Ambient column temperature
3. 200-300 psi system pressure
4. 240 nm UV detection wavelength

A retention time of approximately 2.2 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3.

8.4.4 A 20-microliter aliquot of the sample solution is injected into the liquid chromatograph. The sample may be injected directly by syringe or fixed volume sample loop provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected. Desorption is done in a 5-ml sample volume to provide an adequate volume for rinsing the syringe between injections of different solutions.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and the results are read from a standard curve prepared as discussed in Section 9. Peak heights were found to be an unacceptable method of response measurement.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of XAD-2 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at a sample loading equivalent to the OSHA standard level.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of quinone found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of quinone found in the samples analyzed.

The analytical samples are prepared as follows: XAD-2, equivalent to the amount in the front section (100 mg), is measured into a 12-ml vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of quinone in 20% ethanol in hexane (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µl aliquot is used to prepare the analytical samples.

Note: An ultrasonic cleaner may be needed to break up large particles of quinone.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5, 1 and 2 times the OSHA standard) were prepared by adding an amount of quinone equivalent to that present in a 24-liter sample at the selected level. A stock solution containing 4.95 milligrams of quinone per milliliter of 20% ethanol in hexane was prepared. One, 2 and 4-microliter aliquots of the solution were added to the XAD-2 resin tubes to produce samples equivalent to 24-liter collections at 0.5, 1 and 2 times the OSHA standard level. The analytical samples were allowed to stand at least overnight to assure complete adsorption of the analyte onto the resin. A parallel blank tube was treated in the same manner except that no sample was added to it.

The procedure described can be used to prepare the analytical samples which are analyzed to determine the desorption efficiency over the concentration range of interest.

8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5. Calibration standards are prepared by adding the appropriate volume of spiking solution to 5.0 ml of 20% ethanol in hexane with the same syringe used in the preparation of the samples. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in µg recovered from the tube divided by the weight in µg added to the tube or

$$\text{D.E.} = \frac{\text{Average Weight (µg) Recovered - Blank (µg)}}{\text{Weight (µg) Added}}$$

The desorption efficiency may be dependent on the amount of quinone collected on the resin. Plot the desorption efficiency versus weight of quinone found. This curve is

used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

9.1 Add 5.0 ml of 20% ethanol in hexane to a 12-ml vial. Add aliquots of the same solution as described in Section 8.5.2 to prepare calibration standards or alternatively aliquots of the same solution could be diluted to the appropriate volume. The concentration of standards can be expressed in terms of µg of quinone per 5 ml of 20% ethanol in hexane.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in µg/5 ml.

It has been determined that solutions of quinone in 20% ethanol in hexane are unstable. To insure reliable results it is imperative that all solutions be analyzed within an hour of desorption or preparation. In addition, to minimize the effect of variation in detector response, standard solutions should be analyzed at the same time as sample solutions.

10. Calculations

10.1 Read the weight in units of µg of quinone corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 5.0 ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in front (100-mg) sample section

µg blank = µg found in front (100-mg) blank section

A similar procedure is followed for the backup (50-mg) section.

10.3 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube.

Divide the total weight by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sample flow rate

t = sampling time

P_1 = atmospheric pressure during calibration of sampling pump (mm Hg)

P_2 = atmospheric pressure of air during sampling (mm Hg)

T_1 = ambient temperature during calibration of sampling pump (°K)

T_2 = ambient temperature of air sampled (°K)

10.6 The concentration of quinone in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (see Section 10.4)}}{\text{Sampling Volume (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{108.1} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

108.1 = molecular weight of quinone

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.2 Backup Data Report for Quinone, No. S181, prepared under NIOSH Contract No. 210-76-0123.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Sampling Data Sheet No. S181
September 30, 1977

Substance

Quinone

Standard

8-hour time weighted average: 0.4 mg/cu m

Analytical Method

A known volume of air is drawn through an XAD-2 resin tube to trap the quinone vapors present. The quinone is desorbed from the resin with 20% ethanol in hexane, and the sample is analyzed by high pressure liquid chromatography with UV detection at 240 nm. The method has been validated over the range of 0.017-0.75 mg/cu m for a 24-liter sample at 25°C and 767 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The sampling equipment needed consists of an XAD-2 resin sampling tube and a personal sampling pump calibrated with a representative resin tube in the line. The pump flow rate should be determined accurately to within ±5%, at 0.2 liter per minute. A suitable tube holder should be used to protect the worker from the sharp edges of the glass sampling tube.

The resin tube used to collect the sample consists of a glass tube, cap sealed at both ends, 10-cm long with a 6-mm O.D. and a 4-mm I.D., packed with two sections of (20/50) mesh XAD-2 resin. The two sections include a front section containing 100 mg of resin and a backup section containing 50 mg. The two sections are separated by a plug of silylated glass wool and both the inlet and outlet ends of the tube are also plugged with silylated glass wool. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute.

Sample Size

A sample size of 24 liters is recommended. Sample at a known flow rate between 0.2 and 0.01 liter per minute.

Sampling Procedure

1. Immediately before sampling, the plastic caps at the ends of the tubes should be removed.

2. The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump. The resin tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the front section of the resin tube.

4. A low flow rate pump is used. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. The resin tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

6. One resin tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every batch of 10 samples.

7. Unused, capped sampling tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples, because desorption efficiency can vary from one batch or resin to another. Record the batch number of the resin used.

Special Considerations

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Due to the high resistance of the resin tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than 8 hours of sampling should be done without first fully recharging the battery.

3. Arrange to have the samples analyzed within seven days. Minimize exposure to light and refrigerate samples.

Shipping Instructions

Capped resin rubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

Reference

Quinone, NIOSH Method No. S181.

Backup Data Report No. S181
September 30, 1977

Substance: Quinone

OSHA Standard: 0.4 mg/cu m

Chemical Used for Validation: Quinone, Purified, Fisher Scientific Co.

General Considerations

The method for quinone has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 $\pm$10% and $\overline{CV}_T$ must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for quinone consisted of the following experimental studies:

- Development of a high pressure liquid chromatographic method for analysis of quinone,
- Evaluation of quinone stability in solution,
- Analysis of a total of 18 samples (6 at each of the three test levels--0.5, 1 and 2 times the OSHA standard) spiked with the appropriate amount of quinone to represent a sample volume equal to 24 liters,
- Analysis of a total of 18 samples collected from dynamically generated test atmospheres (6 at each of the three test levels--0.5, 1 and 2 times the OSHA standard) for the same sample volume as above,
- Determination of the breakthrough capacity of XAD-2 resin at high relative humidity,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Preliminary Experimentation

During initial experimentation it was found that an HPLC system using 20:80 ethanol:hexane as a carrier solvent with a Partisil^{tm} PXS 10/25 ODS column (normal phase) could be utilized for the analysis of quinone. The UV detector was set at 240 nm, the UV/absorption maximum for quinone. With this system, quinone was separated chromatographically from hydroquinone, a possible interference.

A limited number of solid sorbents were then tested for desorption of quinone using 20:80 ethanol:hexane. At a loading of 24.6 µg, representing a one-hour collection at 1 liter per minute at the OSHA standard, Lots 104, 105 and 106 charcoal showed no recovery of quinone when desorbed with 1 ml of solvent. XAD-2 and Tenax GC showed acceptable recoveries. XAD-2 was chosen for further studies since fine particles associated with Tenax GC required that the solution be filtered prior to injection. In addition it was found necessary at this point to increase the amount of solvent for desorption to 5 ml. This allowed a more complete rinsing of the syringe used to load the sample solution into the sample loop and reproducibility was improved.

The question of storage stability was then addressed by analyzing samples spiked with an amount of quinone equivalent to a 60-liter collection at the OSHA standard and stored for seven days. These were to be compared with similar samples analyzed after overnight storage. The results are shown in Table S181-1. The mean recoveries indicated a possible loss of 8.1% upon storage, within the acceptable 10% range for this program.

The capacity of 100 mg of XAD-2 was then tested and indicated that a two-hour collection at 0.2 liter per minute would be possible. A set of spiked samples was prepared to represent this collection. The results of the analysis of these samples are shown in Table S181-2 and are quite different from those in Table S181-1. This was later attributed to differences in the total time of analysis, the full set in Table S181-2 taking 3 times longer. Subsequent generation experiments showed high recoveries for an XAD-2 collection/HPLC analysis compared to an isopropanol impinger collection/UV analysis. This indicated that perhaps the desorption efficiency data in Table S181-2 was inaccurate and that an adjustment in the analytical method was needed.

During the analysis of the generated samples mentioned above it was noticed that the height of quinone peaks decreased significantly within a short period of time. It was later found, however, that the areas of these peaks did not decrease similarly. For this reason it was believed that chromatographic conditions were changing. In order to insure that quinone was sufficiently stable in the solvent used,

Table S181-1

Storage Stability of Spiked Samples

Quinone

Analyzed After 1 Day			Analyzed After 7 Days		
µg added	µg found	Recovery	µg added	µg found	Recovery
23.45	23.25	0.991	23.45	19.83	0.846
23.45	22.50	0.959	23.45	21.12	0.901
23.45	22.50	0.959	23.45	21.39	0.912
23.45	23.25	0.991	23.45	21.39	0.912
23.45	23.25	0.991	23.45	21.60	0.921
23.45	23.25	0.991	23.45	21.51	0.917
n =		6			6
mean		0.980			0.902
std dev		0.0165			0.0280
CV_1		0.0169			0.0310

Table S181-2

Data Sheet: Quinone, No. S181

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
4.84	4.29	0.886	9.68	8.28	0.855	19.36	17.38	0.898
4.84	3.83	0.791	9.68	7.92	0.818	19.36	16.13	0.833
4.84	3.86	0.798	9.68	7.61	0.786	19.36	16.06	0.830
4.84	4.03	0.833	9.68	7.63	0.788	19.36	15.75	0.814
4.84	3.98	0.822	9.68	8.13	0.840	19.36	16.41	0.848
4.84	3.89	0.804	9.68	8.30	0.857	19.36	16.94	0.875
n =		6			6			6
mean		0.822			0.824			0.850
std dev		0.0349			0.0319			0.0314
CV_1		0.0425			0.0387			0.0369

CV_1 0.0394

several standard solutions were prepared and analyzed over a period of time. The results are given below in Table S181-3.

Table S181-3

Stability of Quinone in 20:80 Ethanol/Hexane

Solution	Conc. (µg/5 ml)	Initial Area*	Area at 60 min.	Percent Decrease	Area at 90 min.	Percent Decrease	Area at 120 min.	Percent Decrease
1.	20.30	42.15	41.10	2.5	40.60	3.7	39.8	5.6
2.	20.17	42.10	40.40	4.0	39.00	7.4	37.4	11.2
3.	18.43	38.95	38.20	1.9	37.35	4.1	36.3	6.8
4.	18.43	38.95	37.90	2.7	36.70	5.8	35.2	9.6
5.	18.43	38.30	37.25	2.7	36.25	5.4	35.0	8.6

* All areas in arbitrary units.

UV scans were taken of both fresh and 1-day-old solutions. The scan of the 1-day-old solution showed the presence of a peak at 290 nm, the maximum for hydroquinone. No such peak was observed in the spectrum of the fresh solution (30 minutes old).

Based on the data in Table S181-3 it was decided that all solutions should be analyzed within one hour so that any loss due to instability would be kept to a minimum. The average decline in peak area within this time period was found to be 2.8%. Analysis of any samples after one hour could produce unreliable results as reflected in the low recoveries found initially for collection of quinone on XAD-2.

The low recoveries also cast doubt upon the first breakthrough test conducted. Thus the validation procedure was reinitiated from this point and all analyses were performed on samples within one hour of desorption. All standard solutions analyzed were also less than one hour old as well.

In conjunction with the above stability studies, experiments were performed to determine the proper mode of overnight column storage. Previously the column was stored in hexane overnight and it was felt that the transition from pure hexane to 20% ethanol in hexane may have been responsible for the varying chromatography. Decreasing peak heights were observed and were not reflected in area measurements of the same peaks. For this reason the column was stored overnight in the carrier solvent, 20% ethanol in hexane. After this was done, peak heights and areas correlated more closely, although it should be noted

that peak height was still not found to be an acceptable method of measuring detector response.

Principle of the Method

The method validated for the analysis of quinone in air is based on collection on 100 mg of XAD-2 resin, desorption with 20% ethanol in hexane, and analysis of the resulting solution by high pressure liquid chromatography with UV detection at 240 nm. A sample size of 24 liters is recommended.

Analysis

The details of the equipment and instruments used for the analysis and the general approach used are described in Attachment A.

A detailed description of the procedure for analysis, the preparation of analytical samples for the determination of desorption efficiency, and the preparation of calibration standards are given in NIOSH Method No. S181 (Reference 3).

The reliability of the analytical method was tested based on the analysis of 18 analytical samples. These samples were prepared by spiking 100 mg of XAD-2 resin with known aliquots of quinone in 20% ethanol in hexane. The aliquots (1, 2, 4-microliters) added contained respectively 4.95, 9.90 and 19.80 micrograms of quinone representing the equivalent of a 24-liter air sample at 0.5, 1 and 2 times the OSHA standard.

The data for the full set of 18 analytical samples are shown in Table S181-4.

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachment B. Quinone vapor was produced by adding quinone to the generation tower as shown in Figure S181-B-2. At room temperature nitrogen was passed through the tower at a controlled flow of 110 ml/min. At these conditions a reproducible level of quinone vapor was produced within the dilution/sampling system.

The samples were collected using tubes packed with 100 mg of XAD-2 resin, 20/50 mesh, described in Section 6.1.2 of NIOSH Method No. S181. Eighteen samples, six at 0.5, 1 and 2 times the OSHA standard, were collected at 0.2 liters per minute for 120 minutes (24 liters). Note that six samples at the OSHA standard level were also collected at this time for the independent method of determining the generation concentration. The 18 samples were analyzed as described in Section 8.4 of NIOSH Method No. S181. The backup sections of samples collected at 2 times the OSHA standard level were analyzed similarly.

The data for these 18 samples are shown in Table S181-5. It should also be noted that only in one sample was quinone detected in the

Table S181-4

Data Sheet: Quinone, No. S181

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
4.95	5.12	1.034	9.90	9.67	0.977	19.80	19.37	0.978
4.95	5.24	1.059	9.90	9.64	0.974	19.80	19.03	0.961
4.95	4.43	0.895	9.90	9.92	1.002	19.80	18.98	0.959
4.95	4.18	0.844	9.90	8.99	0.908	19.80	17.65	0.891
4.95	5.16	1.042	9.90	9.21	0.930	19.80	17.93	0.906
4.95	4.52	0.913	9.90	9.35	0.944	19.80	18.60	0.939
n =		6			6			6
mean		0.965			0.956			0.939
std dev		0.0914			0.0347			0.0341
CV_1		0.0947			0.0363			0.0363

$\overline{CV}_1$ 0.0622

$\overline{CV}_{A+\overline{DE}}$ 0.0672

Table S181-5

Data Sheet: Quinone, No. S181
Sampling and Analysis

Test Level	Found			Taken	
	µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.31	27.21	0.1584	0.1701	
	4.03	22.22	0.1814	0.1701	
	3.75	22.69	0.1653	0.1701	
	4.11	22.19	0.1852	0.1701	
	3.51	26.50	0.1325	0.1701	
	3.98	22.57	0.1763	0.1701	
		n = 6			
		mean	0.1665		0.979
		std dev	0.01945		
		CV_2	0.1168		
1S	8.27	22.81	0.363	0.374	
	8.35	21.74	0.384	0.374	
	8.16	21.62	0.377	0.374	
	10.40	27.09	0.384	0.374	
	8.55	22.57	0.379	0.374	
	8.76	23.05	0.380	0.374	
		n = 6			
		mean	0.378		1.011
		std dev	0.00778		
		CV_2	0.02058		
2S	19.00	26.26	0.724	0.749	
	16.78	22.22	0.755	0.749	
	16.01	21.62	0.741	0.749	
	16.31	21.86	0.746	0.749	
	17.81	22.93	0.777	0.749	
	16.96	22.46	0.755	0.749	
		n = 6			
		mean	0.750		1.001
		std dev	0.01761		
		CV_2	0.02348		
		$\overline{CV}_2$	0.0698		

Table S181-6

Quinone, No. S181

Data Sheet: Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	----------Found----------			-------Taken*--------	
	µg	Liters	mg/cu m	mg/cu m	Recovery
	8.73	23.61	0.370	0.370	
	9.04	23.45	0.386	0.370	
1S	6.42	16.66	0.385	0.370	
	7.62	20.00	0.381	0.370	
	8.70	22.45	0.388	0.370	
	9.22	23.82	0.387	0.370	
		mean	0.383		1.035
		std dev	0.0067		
		CV_2	0.0175		

Expt. B: Samples Stored 7 Days

	8.63	24.88	0.347	0.370	
	7.98	23.62	0.338	0.370	
1S	7.97	22.88	0.348	0.370	
	7.83	23.69	0.331	0.370	
	9.71	28.64	0.339	0.370	
	8.57	23.38	0.367	0.370	
		mean	0.345		0.932
		std dev	0.0125		
		CV_2	0.0362		

* Taken value based on the amount of quinone lost from the generation tower over a measured period of time (see Attachment B).

backup section. The amount detected was less than 0.5% of the total and is consistent with the data obtained from breakthrough tests.

Storage Stability Studies

Studies were done to assess the stability of quinone upon storage for seven days at atmospheric conditions. For the stability experiments two sets of six samples were collected simultaneously at the OSHA standard level. The data for these samples are given in Table S181-6. The data in Table S181-6 show that the six samples stored for eight days meet the criterion for acceptance, i.e., the mean of six samples stored at room temperature for seven days should be within ±10% of the set analyzed at the beginning of the storage period. In this case, the two means agree within 9.9% indicating adequate stability upon storage. Further evidence of adequate stability is given in Table S181-1.

Breakthrough Tests

A breakthrough test was performed at a relative humidity of at least 81%. Details of generating an atmosphere containing high relative humidities are given in Attachment C.

Breakthrough is defined as the time that the effluent concentration from the collection tube containing 100 mg of XAD-2 reached 5% of the concentration in the test gas atmosphere. 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, when the substance of interest in the test atmosphere is at 2 times the OSHA standard level.

To determine the breakthrough capacity, six resin tubes were mounted on the generating system. Sampling was initiated and beginning at 90 minutes one sample was removed every thirty minutes over a period of four hours. The results summarized in Table S181-7 show that 1.6% breakthrough was observed at the end of four hours, and that a sampling period of 120 minutes at 0.2 liter per minute meets the criterion stated.

Independent Verification of Generator Concentration

The concentration of quinone produced by the vapor generation/dilution system was verified by an independent collection and analysis. Quinone vapor was collected at a rate of 1 liter per minute in midget impingers containing 15 ml of isopropanol (Burdick and Jackson, distilled-in-glass). The resulting solutions were analyzed by UV spectrophotometry at a wavelength of 240 nm using a Perkin-Elmer Coleman Spectrophotometer. As can be seen in Table S181-8, the collection efficiency of the impingers was determined to be 87% at a concentration of 0.374 mg/cu m of quinone. The stability of these solutions has been previously determined (Reference 4). Six samples for this method and the 18 samples

Table S181-7

Breakthrough Test for 100 mg 20/50 Mesh XAD-2
at 0.2 liter per minute

Quinone

-----µg Found-----		Sampling Time	Sampling Volume		% Break-
Front	Back	(mins)	(liters)	mg/cu m[/]	through
15.33	N.D.*	90	19.87	0.772	0.00
17.52	N.D.*	120	22.36	0.784	0.00
21.93	0.035	150	27.23	0.807	0.16
26.28	0.100	183	33.7	0.783	0.38
32.1	0.220	210	40.6	0.796	0.68
36.5	0.585	240	45.2	0.820	1.57
			Avg. Test Conc.	0.794	

* N.D. = Not detectable; detection limit was 0.01 µg/5 ml which corresponds to a maximum of 0.06% breakthrough after 90 minutes.

/ Collection and UV analysis of isopropanol impinger solutions gave an average value of 0.701 mg/cu m. This low value is due to the collection of water, a process which was not duplicated in the standard or blank matrix.

Table S181-8

Collection Efficiency: Collection of Quinone in 15 ml of Isopropanol at 1 liter per minute.

Quinone

µg Found			
Front	Backup	Total	% Collected in Front
23.16	2.52	25.68	90.2
22.85	3.44	26.29	86.9
25.78	7.14	32.9	78.4
21.31	2.52	23.83	89.4
24.24	3.13	27.37	88.6
23.78	2.67	26.45	89.9

Average Collection Efficiency 87.2%

Table S181-9

Comparison of Validated Method and Independent Method

Quinone

Found by HPLC	Found by UV Analysis		
mg/cu m[1]	µg	Liters	mg/cu m
0.363	25.68	71.1	0.361
0.384	26.29	72.5	0.363
0.377	32.9	67.4	0.488*
0.384	23.83	62.5	0.381
0.379	27.37	70.7	0.387
0.380	26.45	69.8	0.379
n = 6			n = 5
mean 0.378			mean 0.374
std dev 0.00778			std dev 0.01154
CV_2 0.02058			CV_2 0.0309

(1) Refer to Table S181-5 for detailed information.

* This value excluded from statistical analysis based on Grubb's test for rejection.

in Table S181-5 were collected simultaneously and are presented in Table S181-9 together with the summarized data from the validated method. The mean value for the collected samples analyzed by UV spectrophotometry is used as the "taken" value at the OSHA standard level in Table S181-5. The "taken" values at 0.5 and 2.0 times the OSHA standard were calculated based on measured dilution ratios of 0.227, 0.499 and 1.000 for generation levels of 0.5, 1.0 and 2 times the OSHA standard.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and summarized in Appendix C and the data in Tables S181-4 and S181-5.

Bartlett's test for the homogeneity of variances was applied to the coefficients of variation in Table S181-5. The data failed, giving a chi squared value of 16.49. The CV_2 used in the calculation of CV_T, however, is based upon pooled data. This is because it appears that, from Tables S181-4 and S181-5, the CV's associated with the 0.5S level may reflect a real phenomenon. Using just the CV_2 for the OSHA standard level would give an unrealistically low value for CV_T and it is felt that using CV_2 based on pooled data is more realistic.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$\overline{CV}_1 = 0.0622$ $\overline{CV}_2 = 0.0698$ $\overline{CV}_T = 0.0847$

The accuracy of the method was determined by comparison of the average value found by analysis of each set of 6 samples at each of the three test levels with the taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 99.7%.

	---- mg/cu m ----		
Test Level	Taken	Found	Agreement (Found÷Taken)
0.5S	0.0420	0.0404	0.979
1S	0.0901	0.0893	1.011
2S	0.1843	0.1786	1.001
		Average =	0.997

The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method as tested. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test, described in the appropriate sections. However, it must be emphasized that the storage stability of quinone on XAD-2 is suspect at room temperature. Even though all experiments evaluating storage stability indicate less than 10% loss after 7 days, the losses observed do indicate that strict precautions should be taken in storing quinone samples. To ensure that the required accuracy is maintained after storage, the samples should be kept from light and heat and, if possible, refrigerated.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

2. Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD) to Deputy Director, DLCD, dated 1/6/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

3. NIOSH Method No. S181, Quinone, prepared under NIOSH Contract No. 210-76-0123 with validation date 9/30/77.

4. Failure Report on Quinone, No. S181, prepared under NIOSH Contract CDC-99-74-45, 1974-1976.

ATTACHMENT A

LIQUID CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the high pressure liquid chromatography (HPLC) method consists of the following:

1. Waters Associates Inc. Model 6000 A Solvent Delivery System,

2. Schoeffel Instrument Corp. SF 770 Monitor Spectroflow and GM 770 Monochromator,

3. Rheodyne Model 7120 Syringe Loading Sample Injector,

4. Spectra Physics System I Computing Integrator.

The Waters Associates Model 6000 A solvent delivery system is especially designed and optimized for liquid chromatography. Constant pulseless flow is achieved with a pair of specially driven positive displacement pumping heads. Flow control is achieved by digital dials in 0.1 ml/min intervals with a range of 0.1 to 9.9 ml/min. Pressurization from 0 to 6000 psig is standard.

A Schoeffel Model SF 770 detection system is used. The SF 770 is a double-beam variable wavelength UV-VIS detector capable of monitoring from below 200 nm to 630 nm. Absorbance ranges of 0.01 to 2.0 are available as well as 1-100% T.

Sample injection is achieved with the Rheodyne Model 7120 syringe loading sample injector. Sample loops, available in 10-100 µl sizes, are filled manually by syringe.

Two injection techniques can be used with this sampling device; either full or partial filling of the sample loop. In this program the sample loop is filled completely to improve reproducibility. The sample loop is rinsed with carrier solvent between injections in order to prevent cross contamination and insure that maximum reproducibility is maintained. This is vitally important since the external (absolute area) standard method is used.

All peak area measurements were done with the System I computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System I also has the capability to calculate sample concentration directly once the calibration factor has been determined.

ATTACHMENT B

VAPOR GENERATION/DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S181-B-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 sampling devices 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, 0.017 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

The desired test concentration of vapors can be produced by either one of the following methods depending on the physical state of the analyte and the mode of introduction into the Main Line.

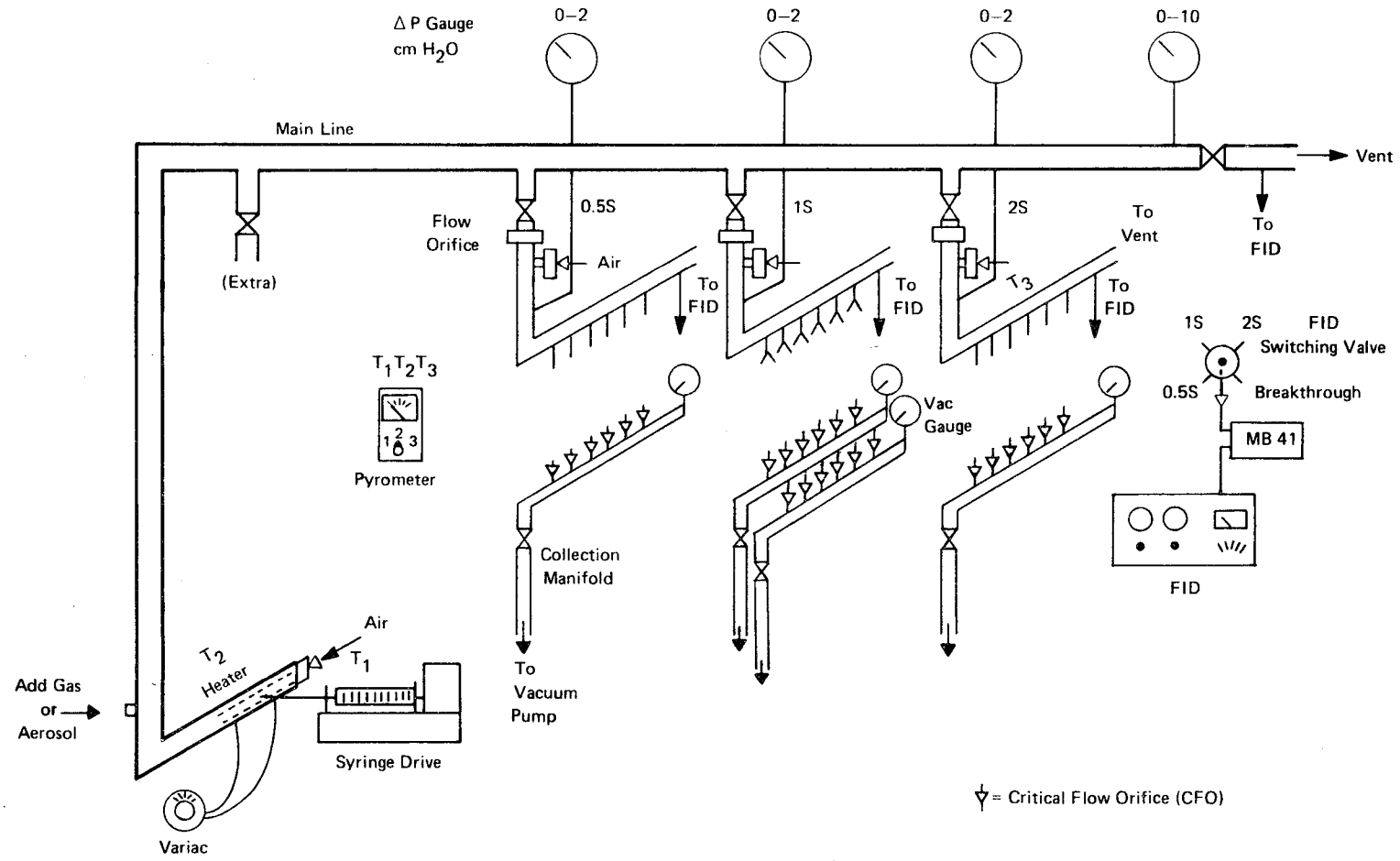


Figure S181-B-2 Vapor Generation/Dilution/Sampling System

- as a gas such as from a gas cylinder via an orifice or other flow controller,

- as a liquid via a syringe injector or as liquid coated on a solid and handled as below,

- as a solid by packing in a glass tower with fritted disc and purging with nitrogen or air.

When a gas cylinder is used, the gas is simply fed into the generator via an orifice or a flow controller usually through a gas rotameter. The gas delivery rate into the Main Line is measured by calibration using a soap-bubble flow meter or a dry gas test meter.

Vapor concentrations from liquids 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 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 can be applied to the heater to assure steady and complete vaporization of the liquid. The delivery rate into the Main Line is determined as described in the calibration section.

To generate vapor test atmospheres from solids with sufficiently high vapor pressure such as naphthalene, antimony trichloride, etc, the unit shown in Figure S181-B-2 is used. The solid is placed in the glass tower above a fritted glass disc which disperses the air or nitrogen stream flowing into the chamber. The amount of material being vaporized into the generator Main Line can be regulated by controlling the flow rate of the nitrogen or air purging into the glass tower. The delivery rate into the Main Line can be determined by weighing the tower before and after the generation process and measuring the time interval for the process.

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 sampling devices connected to the dilution lines is established by connecting each device 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

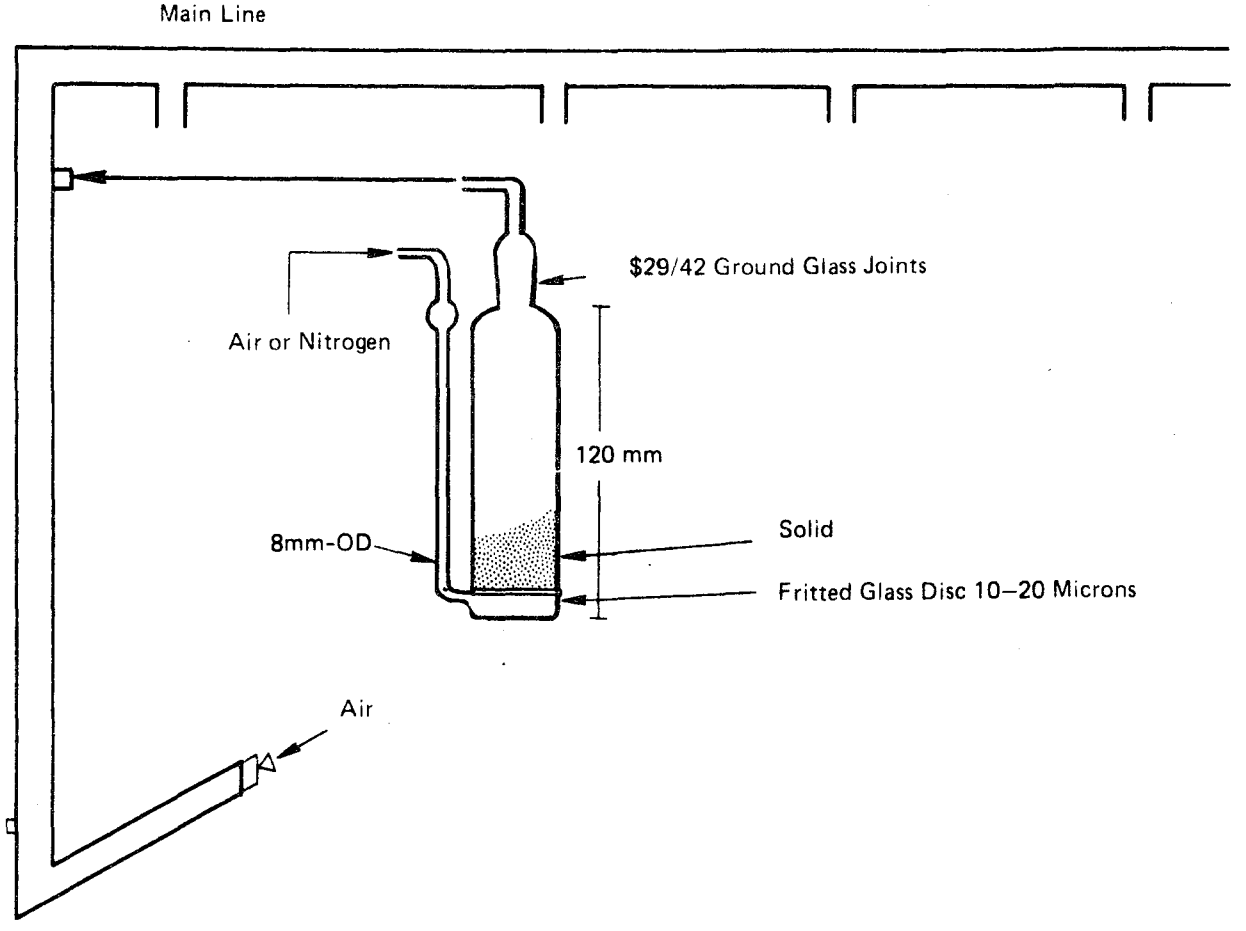


Figure S181-B-2 Vapor Generator for Solids

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 (1.5-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.

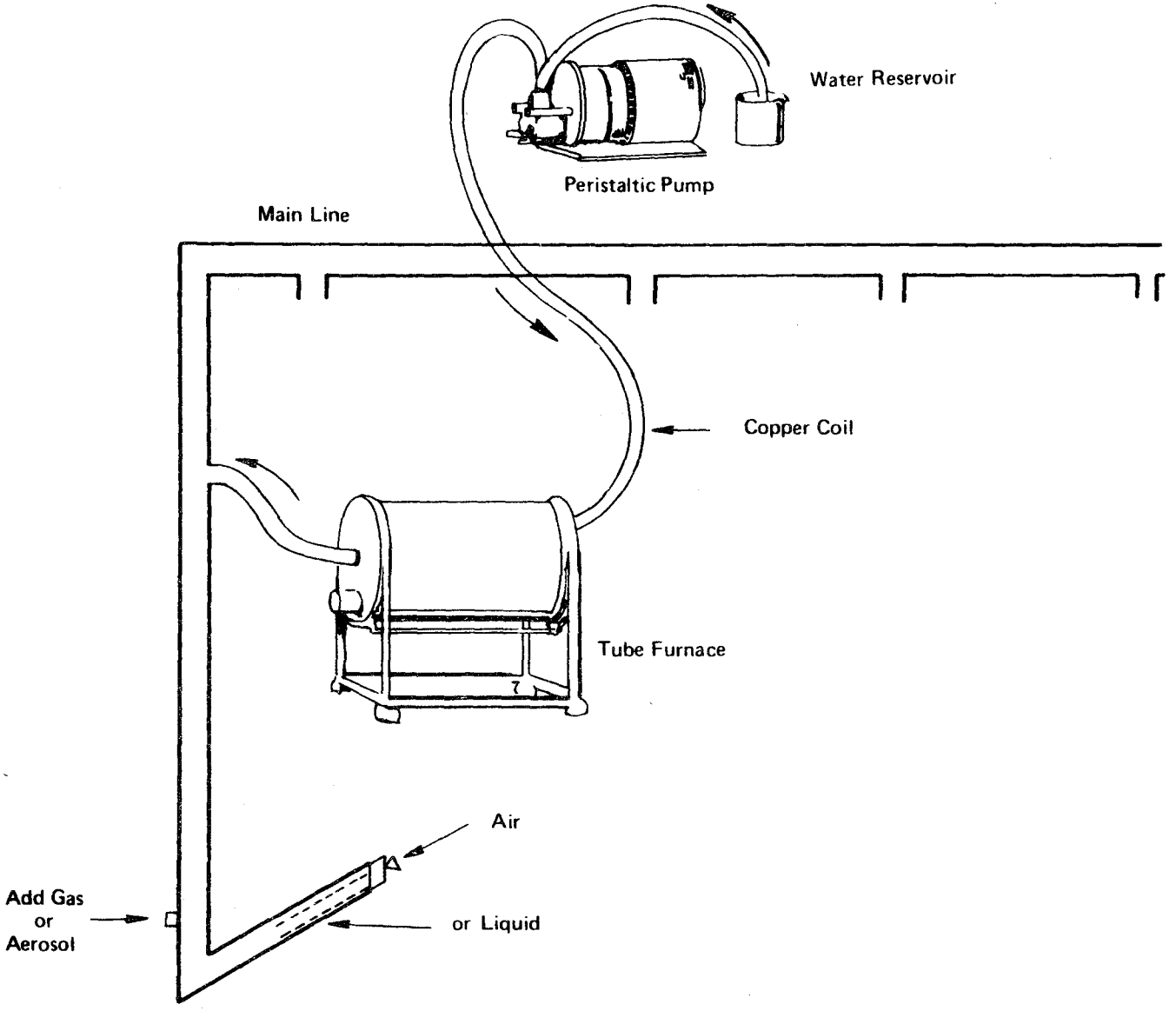


Figure S181-B-3 Generation of High Humidity Atmospheres

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.

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

$\overline{CV}_{A+\overline{AMR}}$ - 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).

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

$\overline{CV}_2$ - 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:

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

In cases where $\overline{CV_2} < \overline{CV_1}$, take $\overline{CV_s} = 0$, and replace $\overline{CV_1}$ by a pooled estimate ($\overline{CV_1}^*$) based on $\overline{CV_1}$ and $\overline{CV_2}$:

$$\overline{CV_T} = \sqrt{(\overline{CV_2})^2 + 0.1667\ (\overline{CV_1}^*)^2 + (0.05)^2}$$

where:

$$\overline{CV_1}^* = \sqrt{\frac{f_1\ (\overline{CV_1})^2 + f_2\ (\overline{CV_2})^2}{f_1 + f_2}}$$

and f_1 and f_2 are the respective values used in the calculation of $\overline{CV_1}$ and $\overline{CV_2}$.

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:

$$B_1' = \frac{x - \bar{x}}{s} \quad \text{or} \quad \frac{\bar{x} - x}{s}$$

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 Coefficients of Variation

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:

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

where:

$\overline{CV}_2$ = Pooled Coefficient of Variation of 18 generated samples.

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.

Diisopropylamine

Analyte:	Diisopropylamine	Method No.:	S141
Matrix:	Air	Range:	8.5-37.4 mg/cu m
OSHA Standard:	5 ppm (20 mg/cu m)	Precision ($\overline{CV}_T$):	0.075
Procedure:	Collection in 0.1N sulfuric acid impingers, GC/FID	Validation Date:	10/28/77

1. Principle of the Method

1.1 A known volume of air is drawn through impingers containing 0.1N sulfuric acid to trap the amine vapors present.

1.2 An aliquot of the sample solution is neutralized with 0.3N potassium hydroxide and injected into a gas chromatograph equipped with a flame ionization detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 8.5-37.4 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 766 mm Hg using a 120-liter sample volume.

2.2 The upper limit of the range of the method is dependent on the collection efficiency. The method is capable of measuring concentrations higher than that noted in Section 2.1 provided the collection efficiency is adequate. Theoretically, if the efficiency of the impinger remains adequate until 90% of the acid is neutralized, 270 mg of diisopropylamine may be collected. This means that an atmosphere containing as much as 2000 mg/cu m can be reliably measured by this method.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time

data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 8-37.4 mg/cu was 0.075. This value corresponds to a 1.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 A collection efficiency of at least 98% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the impingers was 100.4%. In addition, the samples were found to be stable when stored in the dilute sulfuric acid solution for seven days. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget impingers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.3 The impingers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the impingers during shipping.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

6.1.1 A glass standard midget impinger.

6.1.2 A calibrated personal sampling pump suitable for sampling at 1 liter per minute for 120 minutes. The pump must be accurate to within ±5% at the recommended flow rate. The sampling pump is

protected from splashover or water condensation by a second impinger or bubbler positioned between the exit arm of the impinger and the pump.

6.1.3 Sulfuric acid, 0.1N. Prepare a sufficient amount for collection and transfer of samples.

6.1.4 Pipet, 15-ml or other suitable device for adding 0.1N sulfuric acid to the impingers.

6.1.5 Thermometer.

6.1.6 Barometer.

6.1.7 Stopwatch.

6.2 Gas chromatograph with a flame ionization detector.

6.3 Column, (6-ft x 1/4-in O.D. x 2-mm I.D. glass) packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Sample containers with Teflon-lined caps, 2-ml.

6.6 Microliter syringes, 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots for dilution.

6.7 Volumetric flasks, 25-ml or other convenient sizes for making standard solutions and sample dilutions.

7. Reagents

7.1 Diisopropylamine, 99%.

7.2 Distilled water.

7.3 Sulfuric acid, 0.1N in distilled water.

7.4 Potassium hydroxide, 0.3N in distilled water.

7.5 Isoamyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in 0.3N potassium hydroxide.

7.6 Nitrogen, purified.

7.7 Hydrogen, prepurified.

7.8 Air, filtered compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative impinger in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Pipet 15 ml of 0.1N sulfuric acid into the first midget impinger.

8.3.2 Assemble the sampling train. Put the first impinger in a suitable impinger holder. The outlet of this impinger is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable impinger holder which is attached to the pump. Liquid collected in the trap must never be returned to the first impinger.

8.3.3 The air being sampled should not pass through any hose or tubing before entering the first impinger.

8.3.4 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 120 minutes. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 After sampling, remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1-2 ml of 0.1N sulfuric acid into the midget impinger flask. Repeat this process for liquid collected in the trap. However, do not combine the two solutions in one impinger bottom. Be sure each impinger bottom is properly labeled. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

8.3.6 Attempt to minimize sample spillage. Do not allow the solution level in the first impinger to fall below 10 ml. Replace spilled solution with fresh 0.1N sulfuric acid. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.

8.3.7 With each batch of ten samples submit one midget impinger containing 15 ml of 0.1N sulfuric acid prepared from the same stock as that used for sample collection. This impinger must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this impinger as the blank.

8.3.8 The impingers in which the samples are stored should be shipped in a suitable container designed to prevent damage or leakage in transit.

8.4 Analysis of Samples

8.4.1 Transfer of Sample. Transfer the contents of the impinger into a 25-ml volumetric flask, using 2-3 ml of 0.1N sulfuric acid to rinse the impinger bottle. Add rinse to the volumetric flask, then dilute to the mark with 0.1N sulfuric acid.

8.4.2 Neutralization of Sample. Transfer a 500-microliter aliquot of the acidic sample solution to a 2-ml vial. Add 500 microliters 0.3N potassium hydroxide.

Note: If the internal standard method is used, add the internal standard solution made up in 0.3N potassium hydroxide.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 200°C injector temperature
5. 240°C manifold temperature (detector)
6. 125°C column temperature

A retention time of approximately nine minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately sixteen minutes.

8.4.4 Injection of Sample. A 2-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative

such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Sample Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to 25 ml of 0.1N sulfuric acid. The solutions are then neutralized and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm$ 5%.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 120-liter sample at the selected level was used to determine the analytical method recovery. Six volumetrics at each of the three levels (0.5, 1, and 2X the OSHA standard) were spiked with diisopropylamine. A parallel blank was also prepared except that no sample was added to it. All solutions were then neutralized and analyzed as described in Section 8.4.

The sample recovery equals the average weight in mg recovered from the volumetric divided by the weight in mg added to the volumetric, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The average recovery values obtained were at least 97% and as such no recovery correction factor has been used in the determination of the "true" values.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 25 ml 0.1N sulfuric acid because the samples are in this amount of sulfuric acid. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample in order to minimize the effect of variations in FID response. A calibration curve is established by plotting concentration in mg per 25 ml versus peak area.

For the internal standard method, use 0.3N potassium hydroxide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg/25 ml.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg per 25 ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample solution
mg blank = mg found in blank solution

10.3 Divide the total weight by the analytical method recovery to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sample flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air samples (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Directory, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.2 Backup Data Report for Diisopropylamine, No. S141, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S141

October 28, 1977

Substance

Diisopropylamine

Standard

8-hour time-weighted average: 5 ppm (20 mg/cu m)

Analytical Method

A known volume of air is drawn through a midget impinger which contains 15 ml of 0.1N sulfuric acid. An aliquot of this sample solution is neutralized and injected into a gas chromatograph with a flame ionization detector. This method has been validated over the range of 8.5-37.4 mg/cu m for a 120-liter sample at 24°C and 766 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The following equipment is needed for sampling diisopropylamine: a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at a flow rate of 1.0 liter per minute, a standard midget impinger containing 15 ml of 0.1N sulfuric acid, a trap which is a second impinger or bubbler used to protect the pump from spillage, and an extra impinger solution and distilled water.

Sample Size

A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 120 minutes.

Sampling Procedure

1. Pour 15 ml of 0.1N sulfuric acid into the first impinger.

2. Assemble the sampling train. Put the first impinger in a suitable impinger holder. The outlet of this impinger is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable impinger holder which is attached to the pump. Liquid collected in the trap must never be returned to the first impinger.

3. Air should not pass through any hose or tubing before entering the first impinger.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow

rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. After sampling, remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1-2 ml of 0.1N sulfuric acid into the midget impinger flask. Repeat this process for liquid collected in the trap. However, do not combine the two solutions in one impinger bottom. Be sure each impinger bottom is properly labeled. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

6. Attempt to minimize sample spillage. Do not allow the solution level in the first impinger to fall below 10 ml. Replace spilled solution with fresh 0.1N sulfuric acid. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.

7. With each batch of ten samples submit one midget impinger containing 15 ml of 0.1N sulfuric acid prepared from the same stock as that used for sample collection. This impinger must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this impinger as the blank.

Special Consideration

1. When other air contaminants are known or suspected to be present, such information, including their suspected identities, should be transmitted with the sample.

2. If a significant amount of diisopropylamine is found by the analyst in the trap or if less than 7 ml of solution remains in the first impinger, the sample should be considered invalid.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon-lined cap. Use shrinkable bands or stretchable tape to keep the container tightly sealed. Label of the bulk sample should match air samples for identification purposes. Do not ship sample with the collected samples.

Shipping Instructions

The impingers in which the samples are stored should be shipped in a suitable container designed to prevent damage or leakage in transit.

Reference

Diisopropylamine, NIOSH Method No. S141.

Backup Data Report No. S141
October 28, 1977

Substance: Diisopropylamine

OSHA Standard: 5 ppm (20 mg/cu m)

Chemical Used for Validation: Diisopropylamine, 99%, Aldrich Chemical Company

General Considerations

The method for diisopropylamine has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 $\pm$10% and the $\overline{CV}_T$ of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for diisopropylamine consisted of the following experimental studies:

- Evaluation of a midget impinger containing dilute sulfuric acid relative to collection efficiency at 2X the OSHA standard level,
- Analysis of a total of 18 samples (6 samples at each of the three test levels--0.5, 1 and 2X the OSHA standard) spiked with the appropriate amount of diisopropylamine to represent a sample volume equal to 120 liters,
- Analysis of a total of 18 samples collected from dynamically generated test atmospheres (6 samples at each of the three test levels--0.5, 1 and 2X the OSHA standard) for the same sample volume as above,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following appropriate sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Development of Analytical Method

Based on recommendations in the Diisopropylamine Failure Report (Reference 3), as well as on the success encountered with other amines (Reference 4), initial experiments were aimed at validating a method for diisopropylamine based on collection on sulfuric acid-treated silica gel. Breakthrough tests at 80% relative humidity were conducted first. No breakthrough was observed after sampling for four hours at 0.8 liters per minute on 150 mg of silica gel treated with sulfuric acid. Based on a 120-liter sample volume, eighteen analytical spikes were prepared and eighteen generated samples were collected in a dry environment. Storage stability tests were done on six samples for seven days. All samples were desorbed for one hour in 1 ml of 50% aqueous methanol. The data for these three sets of samples are shown in Tables S141-1 to S141-3.

Although at this point a method had been developed for diisopropylamine which passed all the requirements for validation, a further study was done to examine the possibility of sample dilution due to sampling in a humid environment with sulfuric acid-treated silica gel. Eighteen samples were generated and analyzed as above except that the diisopropylamine was generated in an environment where the relative humidity at the 2S line was measured to be at least 70%.

The recovery values for these humid samples were compared to those of samples generated in a dry environment. The data are summarized in Table S141-4, Experiment A.

These data indicate that sample dilution due to collection of water may in fact be occurring. However, in order for sample dilution to account for the observed 53% recovery approximately 1 ml of water would need to be present in each silica gel tube. This was clearly not the case and other explanations were sought. Before doing this, the extent of sample dilution was ascertained by desorbing samples up to a fixed volume in 2-ml volumetric flasks. The desorption efficiency and precision of this method was determined by desorbing 18 spiked samples in 2-ml volumetric flasks with 50% aqueous methanol for one hour. The average desorption efficiency was found to be 89.9% with a $\overline{CV}_1$ of 3.4%. Two full sets of samples were then collected, one in a dry environment and one in a humid environment, and the two sets of samples analyzed as above. The data from Experiment B, shown in Table S141-4, is quite similar to that in Experiment A, indicating that the effect of sample dilution is minimal. The extremely low recoveries at the 2S level must be explained by other phenomena.

Another possible effect of sampling in a humid atmosphere is a change in solvent composition; the samples collected at high humidity having a higher water content which could alter solubility and/or desorption efficiency. This question was addressed by desorbing one set of six samples collected in a humid environment in distilled water and another set of humid samples in pure methanol. The above phenomenon was again observed, eliminating solvent composition as the problem.

It was stated earlier that no breakthrough was observed after sampling

TABLE S141-1

Data Sheet: Diisopropylamine, No. S141

(150 mg sulfuric acid-treated silica gel; 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
1.155	0.974	0.843	2.310	1.957	0.847	4.76	4.41	0.926
1.155	0.960	0.831	2.310	1.990	0.861	4.76	4.38	0.920
1.155	0.956	0.828	2.310	1.953	0.845	4.76	4.33	0.910
1.155	0.999	0.865	2.310	1.965	0.851	4.76	4.31	0.905
1.155	*	*	2.310	1.998	0.865	4.76	4.46	0.937
1.155	0.987	0.855	2.310	2.017	0.873	4.76	4.48	0.941
n =	5			6			6	
mean	0.844			0.857			0.923	
std dev	0.01571			0.01110			0.01436	
CV_1	0.01860			0.01295			0.01555	

$\overline{CV_1}$ 0.01566

$\overline{CV_{A+\overline{DE}}}$ 0.01691

* Sample lost.

Table S141-2

Data Sheet: Diisopropylamine, No. S141

Sampling and Analysis
(150 mg sulfuric acid-treated silica gel; samples stored 1 day)

Test Level	Found				Taken	
	mg	Corr mg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.808	0.957	129.3	7.40	8.29	
	0.884	1.047	128.4	8.15	8.29	
	0.861	1.020	129.0	7.91	8.29	
	0.956	1.133	128.4	8.82	8.29	
	0.898	1.064	129.9	8.19	8.29	
	0.866	1.026	130.2	7.88	8.29	
			n = 6			
			mean	8.06		0.972
			std dev	0.468		
			CV_2	0.058		
1S	1.996	2.329	129.3	18.01	18.21	
	2.049	2.391	129.9	18.41	18.21	
	2.072	2.418	128.6	18.80	18.21	
	2.028	2.366	129.1	18.33	18.21	
	1.912	2.231	128.0	17.43	18.21	
	1.959	2.286	127.6	17.92	18.21	
			n = 6			
			mean	18.15		0.997
			std dev	0.472		
			CV_2	0.0260		
2S	4.50	4.88	129.7	37.6	36.5	
	4.40	4.77	128.0	37.3	36.5	
	2.586	2.802	128.9	21.74*	36.5	
	4.29	4.65	128.5	36.2	36.5	
	3.99	4.32	129.8	33.3	36.5	
	4.58	4.96	129.9	38.2	36.5	
			n = 5			
			mean	36.5		1.000
			std dev	1.941		
			CV_2	0.053		
			$\overline{CV}_2$	0.0474		

ΔCorrected for DE factor.
*This value excluded from statistical analysis based on the Grubb's Outlier test described in Reference 2.

TABLE S141-3

Data Sheet: Diisopropylamine, No. S141

Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found				Taken	
	mg	Corr mg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
1S	2.128	2.483	131.2	18.92	17.32	
	2.232	2.604	131.8	19.76	17.32	
	2.230	2.602	130.4	19.95	17.32	
	2.047	2.389	130.9	18.25	17.32	
	2.186	2.551	129.8	19.65	17.32	
	2.254	2.630	129.4	20.32	17.32	
			mean	19.48		1.124
			CV_2	0.0388		

Expt. B: Samples Stored 7 Days

1S	1.986	2.317	130.8	17.71	17.32	
	2.058	2.401	133.1	18.04	17.32	
	2.027	2.365	129.1	18.32	17.32	
	2.031	2.370	131.4	18.04	17.32	
	2.095	2.445	130.3	18.76	17.32	
	2.128	2.483	131.0	18.95	17.32	
			mean	18.30		1.057
			CV_2	0.0258		

[Δ]Corrected for DE factor

Table S141-4

Data Sheet: Diisopropylamine, No. S141

The Effect of Relative Humidity on Recovery

Experiment A: Samples desorbed in 1 ml 50% MeOH

Level	% Relative Humidity	----mg/cu m---- Found*	Taken	Recovery	Difference
0.5S	Dry	6.80	8.29	0.820	0.064
	36	6.38	8.44	0.756	
1S	Dry	15.55	18.21	0.854	0.068
	62	14.59	18.56	0.786	
2S	Dry	33.7	36.5	0.923	0.394
	73	19.68	37.2	0.529	

*Uncorrected for desorption efficiency in order to maintain a basis for comparison.

Experiment B: Samples desorbed in 2 ml to volume 50% MeOH

Level	% Relative Humidity	----mg/cu m---- Found*	Taken	Recovery	Difference
0.5S	Dry	6.55	8.44	0.776	0.08
	45	5.83	8.38	0.696	
1S	Dry	16.08	18.56	0.866	0.117
	65	13.79	18.41	0.749	
2S	Dry	33.1	37.2	0.890	0.373
	80	19.09	36.9	0.517Δ	

* Uncorrected for desorption efficiency.

Δ CV > 0.1

for four hours in an 80% relative humidity environment. Furthermore, no diisopropylamine was found in any of the backup sections collected in a dry environment at 2X the OSHA standard level. Thus, from the data gathered at this point, the possibility existed that the low recoveries observed at the 2S level at high humidities were an accurate measure of the diisopropylamine present; in other words, the presence of a large amount of water vapor causes a decrease in the concentration of diisopropylamine. In order to examine this possibility, an atmosphere where the relative humidity was 80% in all three lines was generated with no diisopropylamine present. Eighteen humid air samples were collected at 1 liter per minute for 120 minutes. The silica gel in each tube was transferred to a vial and spiked with known amounts of diisopropylamine in the usual manner. Desorption was done for one hour in 1 ml of 50% methanol. The desorption efficiency for the 0.5, 1, and 2S levels was 0.806, 0.760 and 0.540 respectively. These data indicated that the humidity problem may have been concentration dependent.

In the final experiment, the sample volume was reduced from 120 liters to 24 liters, thereby reducing the amount of diisopropylamine collected. Six 2S samples were collected in an 80% relative humidity environment at a rate of 0.2 liter per minute for 120 minutes. The recovery for these six samples averaged 56.8%. The effect of sample concentration was, therefore, minimal.

The method finally developed for diisopropylamine involves collection in impingers containing dilute sulfuric acid diluted to a fixed volume prior to analysis. In this way, the problems encountered when sampling in a humid atmosphere with acid-treated silica gel are avoided.

Principle of the Method

The method validated for the analysis of diisopropylamine in air is based on collection in impingers containing 15 ml of 0.1N sulfuric acid, neutralization with 0.3N potassium hydroxide, and analysis of the resulting solution by gas chromatography with a flame ionization detector. A sample size of 120 liters is recommended.

Analysis

The details of the equipment and instruments used for the analysis and the general approach used are described in Attachment A.

A detailed description of the procedure for analysis, the preparation of analytical samples for determination of recovery and the preparation of calibration standards are given in NIOSH Method No. S141 (Reference 5).

The reliability of the analytical method was tested based on the analysis of 18 analytical samples. These samples were prepared by spiking 25 ml of 0.1N sulfuric acid with known aliquots of diisopropylamine representing the equivalent of a 120-liter air sample at 0.5, 1 and 2X the OSHA standard.

The data for the full set of 18 analytical samples are shown in Table S141-5.

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachment B. A steady stream of diisopropylamine was delivered via a calibrated syringe drive at a rate of 4.03 mg/min to a dry air stream flowing at a rate of 0.1086 cu m/min. Due to the high reactivity of diisopropylamine with the stainless steel syringe needle, the syringe was connected directly to the generation equipment by means of a small piece of Teflon tubing. Using this approach, a reproducible and steady stream of diisopropylamine vapor was produced in the test chamber. The three sample lines were maintained at measured dilution ratios of 0.227, 0.499 and 1.000 to produce test levels 0.5, 1 and 2X the OSHA standard. The delivery rate of the diisopropylamine was determined by calibrating the syringe drive as described in Attachment C and the data are shown in the section on Independent Method of Verifying Generator Concentration.

The samples were collected as described in NIOSH Method No. S141 using impingers containing 15 ml of 0.1N sulfuric acid. Twenty-four samples were collected simultaneously at 1.0 liter per minute for 120 minutes (120 liters). Eighteen samples, six at each of the three test levels, were analyzed after one day, as described in Section 8.4 of NIOSH Method No. S141: the backup impingers collected at 2X the OSHA standard level were analyzed similarly. The six remaining samples were stored and analyzed after seven days.

The data obtained for the 18 one-day-old samples are shown in Table S141-6.

Storage Stability

Studies were done to assess the stability of diisopropylamine samples upon storage for one week at atmospheric conditions. For these studies, six samples collected at 1X the OSHA standard level were stored for seven days and analyzed and the results compared with the data for six samples collected at 1X the OSHA standard and analyzed after one day. The data for these samples, given in Table S141-7, show that the samples are stable over a seven-day period; the average recovery was 94.2% for the one-day-old samples vs. 94.9% for the seven-day-old samples.

Collection Efficiency

The collection efficiency of midget impingers containing 0.1N sulfuric acid for diisopropylamine was determined at a test concentration of 37.4 mg/cu m for a 120-liter sample. Two impingers containing 15 ml of 0.1N sulfuric acid 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 diisopropylamine in the front impinger relative to the total found in the front and backup impingers

TABLE S141-5

Data Sheet: Diisopropylamine, No. S141

Analysis

Level	0.5S			1S			2S	
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
1.155	1.108	0.959	2.310	2.360	1.022	4.76	4.81	1.010
1.155	1.047	0.906	2.310	2.353	1.019	4.76	4.82	1.013
1.155	1.117	0.967	2.310	2.324	1.006	4.76	4.91	1.032
1.155	1.142	0.989	2.310	2.418	1.047	4.76	4.90	1.029
1.155	1.141	0.988	2.310	2.288	0.990	4.76	4.93	1.036
1.155	1.203	1.042	2.310	2.237	0.968	4.76	4.97	1.044
n =		6			6			6
mean		0.975			1.009			1.027
std dev		0.0446			0.02743			0.01329
CV_1		0.0457			0.02720			0.01294

$\overline{CV}_1$ 0.0316

$\overline{CV}_{A+\overline{AMR}}$ 0.0341

TABLE S141-6

Data Sheet: Diisopropylamine, No. S141

Sampling and Analysis

Test Level	Found			Taken	
	mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	1.122	129.9	8.64	8.49	
	1.058	128.9	8.21	8.49	
	*	129.5	*	8.49	
	1.125	128.9	8.73	8.49	
	0.950	130.5	7.28	8.49	
	0.998	130.7	7.64	8.49	
		n = 5			
		mean	8.10		0.954
		std dev	0.629		
		CV_2	0.078		
1S	2.348	129.5	18.13	18.66	
	2.320	131.8	17.60	18.66	
	2.165	127.8	16.94	18.66	
	2.075	130.1	15.95	18.66	
	2.405	129.0	18.64	18.66	
	2.360	129.7	18.20	18.66	
		n = 6			
		mean	17.58		0.942
		std dev	0.988		
		CV_2	0.056		
2S	4.92	130.2	37.8	37.4	
	5.00	128.6	38.9	37.4	
	4.82	129.4	37.2	37.4	
	5.05	129.0	39.1	37.4	
	4.91	130.3	37.7	37.4	
	4.88	130.5	37.4	37.4	
		n = 6			
		mean	38.0		1.016
		std dev	0.794		
		CV_2	0.0209		
		$\overline{CV}_2$	0.0549		

*Sample lost

TABLE S141-7

Data Sheet: Diisopropylamine, No. S141

Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found			Taken	
	mg	Liters	mg/cu m	mg/cu m	Recovery
1S	2.348	129.5	18.13	18.66	
	2.320	131.8	17.60	18.66	
	2.165	127.8	16.94	18.66	
	2.075	130.1	15.95	18.66	
	2.405	129.0	18.64	18.66	
	2.360	129.7	18.20	18.66	
		mean	17.58		0.942
		CV_2	0.0562		

Expt. B: Samples Stored 7 Days

1S	2.390	129.9	18.40	18.66	
	2.385	130.5	18.28	18.66	
	2.240	129.2	17.34	18.66	
	1.490	129.6	11.50*	18.66	
	2.240	128.6	17.42	18.66	
	2.192	128.1	17.11	18.66	
		mean	17.71		0.949
		CV_2	0.0332		

*This value excluded from statistical analysis based on the Grubb's outlier test as described in Reference 2.

was used as a measure of collection efficiency. The data for six samples, summarized in Table S141-8, show an average collection efficiency of 98.4%.

Independent Method of Verifying Generator Concentration

The method used for independent determination of generator concentration was based on experimentally determining the delivery rate of diisopropylamine (in mg/min) into a measured dilution air flow (in cu m/min). On the basis of these two determined values, the Taken generator concentration at the 2S line can be calculated. The concentration at the 0.5S and 1S line can be calculated by measuring the dilution ratio of the 0.5S and 1S line relative to the 2S (main) line.

For the diisopropylamine generation, the syringe delivery rate was calibrated as described in the calibration section in Appendix B; the data expressed in mg per minute for the replicate determinations are indicated below.

3.94
3.91
4.10
4.10
4.01
4.13

Average = 4.03 mg/min

The corrected main line air flow was determined to be 0.1076 cu m/min at the respective atmospheric temperature and pressure conditions of 24°C and 766 mm of Hg for this generation experiment. In addition, the sample lines were maintained at dilution ratios of 0.227, 0.499 and 1.000 to produce test levels at 0.5, 1 and 2X the OSHA standard.

Based on these data, the Taken generator concentration at the 0.5, 1 and 2S lines are respectively: 8.49, 18.66 and 37.4 mg/cu m.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and summarized in Attachment D and the data in Tables S141-5 and S141-6.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1 and 2X the OSHA standard for diisopropylamine. The data (Table S141-6) gave a chi squared value of 6.07 indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

TABLE S141-8

Data Sheet: Diisopropylamine, No. S141

Collection Efficiency of Diisopropylamine
in 0.1N Sulfuric Acid/Impingers

mg Found			% Collected
Front	Backup	Total	in Front
4.92	0.1062	5.03	97.8
5.00	N.D.	5.00	100.0
4.82	0.1258	4.95	97.4
5.05	0.087	5.14	98.2
4.91	0.1518	5.06	97.0
4.88	N.D.	4.88	100.0

Average Collection Efficiency....98.4

N.D. = Not detectable; the detection limit is estimated to be 2 µg/ml which corresponds to a collection efficiency of approximately 99%.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$$\overline{CV}_1 = 0.0316 \qquad \overline{CV}_2 = 0.0549 \qquad \overline{CV}_T = 0.0754$$

The accuracy of the method was determined by comparison of the average value found by analysis of six samples at each of the three test levels with the Taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 97.1%.

	------mg/cu m-------		Agreement
Test Level	Taken	Found	(Found ÷ Taken)
0.5S	8.49	8.10	95.4
1S	18.66	17.58	94.2
2S	37.4	38.0	101.6
		Average....	97.1%

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

2. Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/76, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

3. Failure Report on Diisopropylamine, No. S141, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

4. n-Butylamine NIOSH Method No. S138, prepared under NIOSH Contract No. 210-76-0123.

5. Diisopropylamine, NIOSH Method No. S141, prepared under NIOSH Contract No. 210-76-0123 with validation date 10/28/77.

ATTACHMENT A

GAS CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the gas chromatography (GC) methods consists of a Varian 2700 Series Gas Chromatograph, a Varian Model 8000 automatic sample injector and a Spectra Physics System 1 computing integrator.

The Varian 2700 is a dual column unit equipped with a flame ionization detector and a photoionization detector (Hnu Systems, Inc.). The unit can be set for isothermal or for linear temperature program operation, either manually or automatically.

The Model 8000 automatic sample injector is mounted horizontally on the Varian 2700 and can readily be moved to align with either of the two injection ports. 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 dry nitrogen, and a control unit which permits total automation in a closed loop form with a computer. For this program, the syringe injector has been set to deliver either 2 or 5 microliters of sample solution. The unit has been tested to verify that sample to sample cross-contamination does not occur and that the reproducibility of the sample injection is adequate. Periodic checks have been carried out on six or twelve repetitive injections of a standard solution in carbon disulfide and the observed standard deviation of the integrated peak areas is never greater than 2.5%.

All peak area measurements were done with the System 1 computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System 1 also has the capability to calculate sample concentration directly once the calibration factor has been determined.

Approach

The internal standard method (relative area measurements) has been used for this program not only because of its inherently better reproducibility than the external standard method (absolute area measurements) but also as a safeguard against any problems that could arise during the periods of unattended overnight operation. Such problems include detector response variations and the partial clogging of the sample injector loop which can give rise to variability in sample size injections. These clogging effects are caused by the very fine solid sorbent particles which remain suspended in the solution.

A comparative study of the reproducibility of the absolute area and the relative area measurements was performed using sec-butyl acetate (1.5 mg/ml) and undecane as internal standard. The precision of 12 successive determinations was 1.7% based on absolute areas and 0.4% using relative areas.

The choice of an internal standard has been restricted to those compounds which present minimal adsorption losses on the specific solid sorbent used. Experiments have been run to verify adsorption losses by determining the integrated areas of analyte and internal standard in a calibration solution and comparing these areas with the respective areas obtained when 1.0 ml (or other appropriate volume) aliquots of the same calibration solution are added to the appropriate amounts of solid sorbent. (Use the same weight of solid sorbent as that used for sampling.) The ideal internal standard is one which does not show any significant decrease in area due to the solid sorbent addition; this phenomenon is dependent on the interactive characteristics of the internal standard, the solid sorbent and the desorption solvent.

ATTACHMENT B

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S141-B-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 sampling devices 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, 0.017 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) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

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

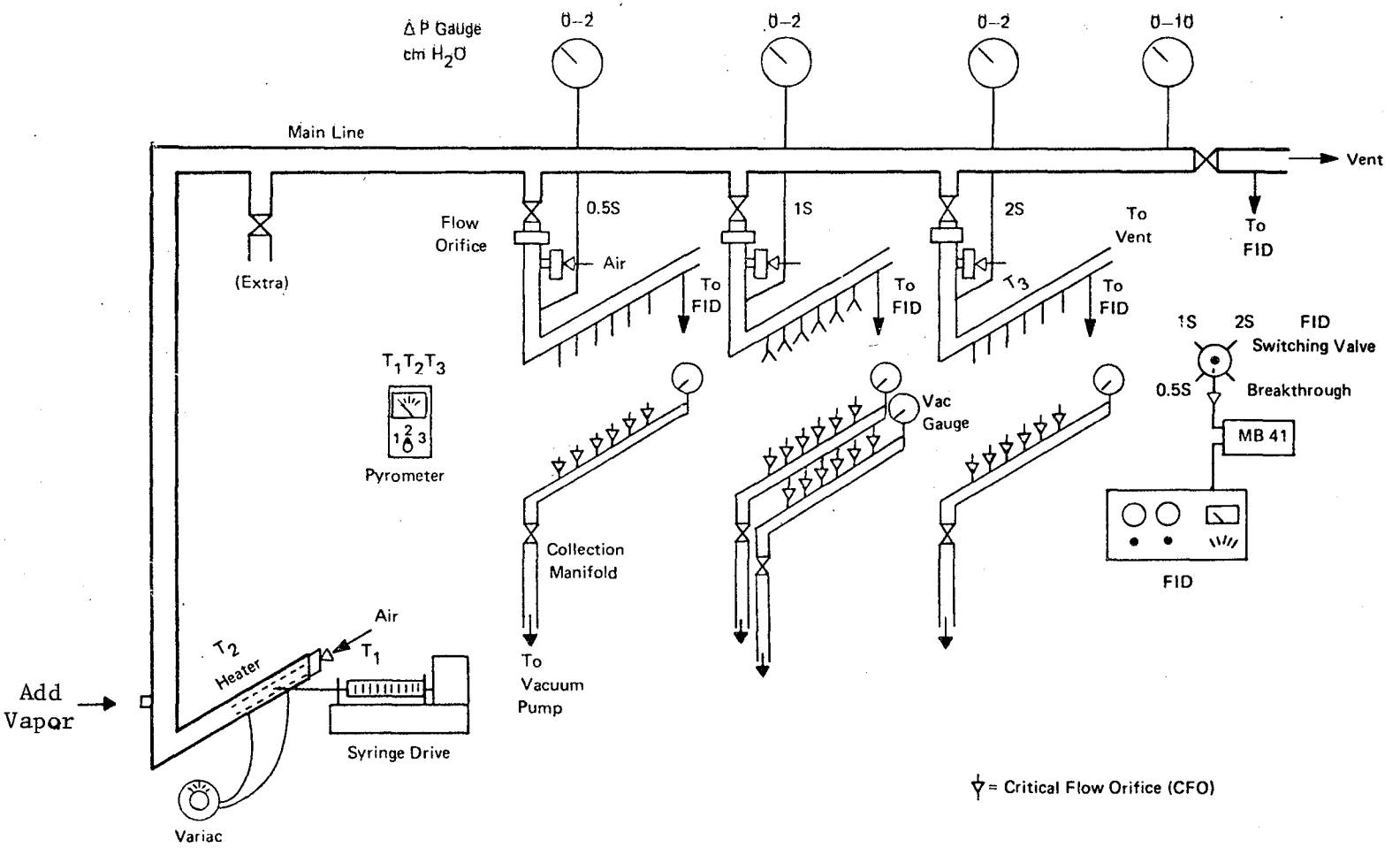


Figure S141-B-1. Vapor Generation/Dilution/Sampling System

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 sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. 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 a 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 (1.5 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

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 0.1086 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.

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	0.499	0.227

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

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. 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. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) 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.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S141-B-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.

2. Sample delivery rate is determined by appropriate calibration.

3. Sample is fed into Main Line until vapor concentration equilibrium is established.

4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.

5. The four sets of six samples from the three concentration levels are collected simultaneously.

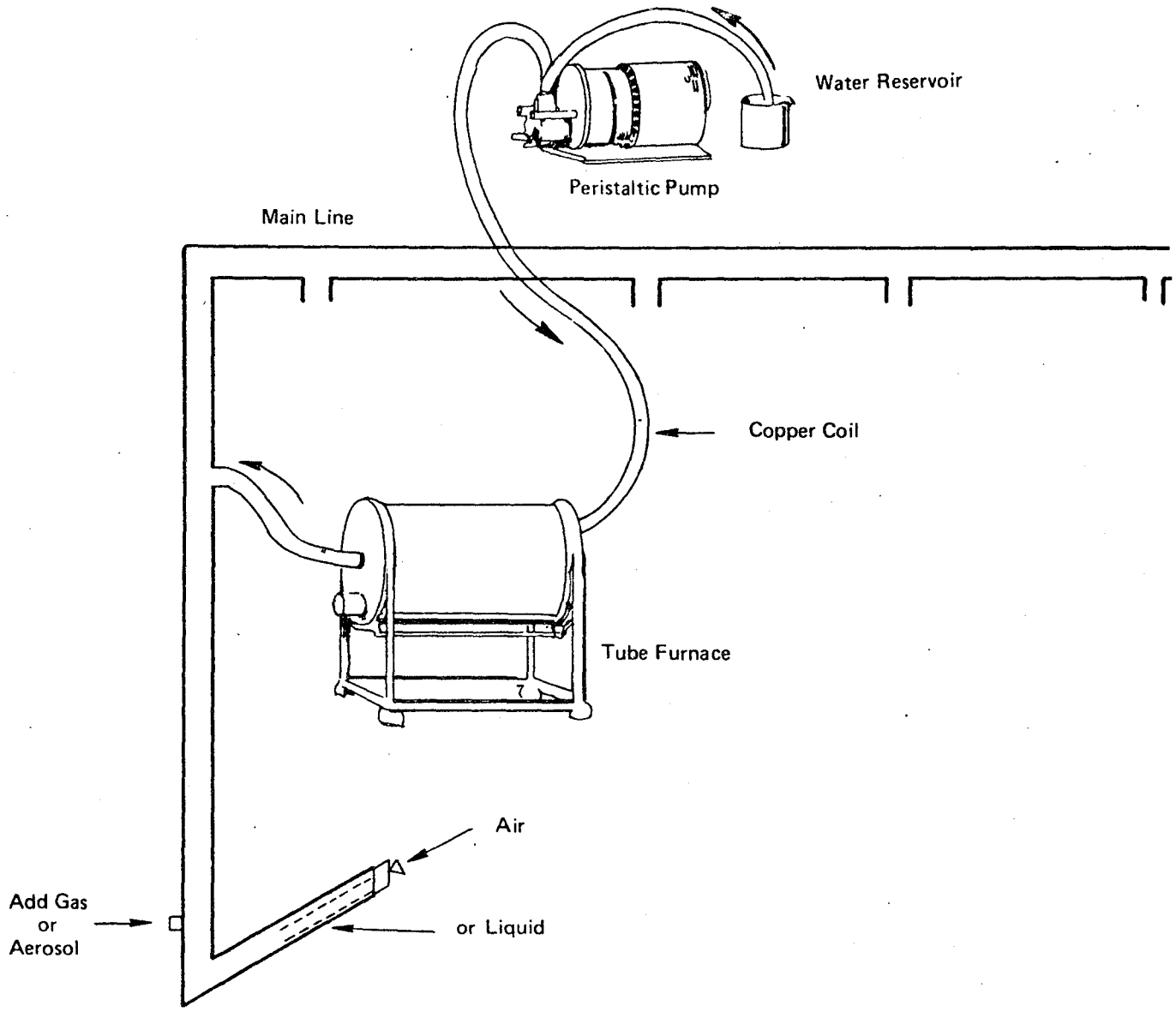


Figure S141-B-2 Generation of High Humidity Atmospheres

ATTACHMENT C

VAPOR GENERATION

Continuous Direct Injection

Vapor concentrations from liquids are generated by adding known amounts of liquid to the Main Line of the vapor dilution/sampling apparatus. A continuous delivery rate is achieved using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25 G stainless steel needle in the Main Line by a short length of 0.16-cm (1/16-in) O.D. Teflon tubing. If the substance of interest is reactive with the stainless steel needle then the Teflon tubing is placed within the Main Line replacing the needle. When dealing with liquids of low volatility the 256 needle is mounted such that the tip of the needle rests inside a 10-cm length of 8-mm I.D. 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.

Calibration of Syringe Delivery

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 25-800 mg are collected depending on the specific compound being studied.

Calculation of Main Line 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.

ATTACHMENT D

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:

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

In cases where $\overline{CV}_2 < \overline{CV}_1$, take $\overline{CV}_s = 0$, and replace $\overline{CV}_1$ by a pooled estimate ($\overline{CV}_1$*) based on $\overline{CV}_1$ and $\overline{CV}_2$:

$$\overline{CV}_T = \sqrt{(\overline{CV}_2)^2 + 0.1667\ (\overline{CV}_1^*)^2 + (0.05)^2}$$

where:

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

and f_1 and f_2 are the respective values used in the calculation of $\overline{CV}_1$ and $\overline{CV}_2$.

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:

$$B_1' = \frac{x - \bar{x}}{s} \quad \text{or} \quad \frac{\bar{x} - x}{s}$$

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 Coefficients of Variation

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:

$$\text{Chi Squared} = \frac{f \ln \left(\overline{CV_2}\right)^2 - \sum_{i=1}^{n} f_i \ln \left(CV_{2i}\right)^2}{1 + \frac{1}{3(k-1)} \left[\left(\sum_{i=1}^{n} \frac{1}{f_i}\right) - \frac{1}{f}\right]}$$

where:

$\overline{CV_2}$ = Pooled Coefficient of Variation of 18 generated samples.

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.

Diphenyl

(Biphenyl)

Analyte:	Biphenyl	Method No.:	S24
Matrix:	Air	Range:	0.64-2.4 mg/cu m
OSHA Standard:	0.2 ppm (1 mg/cu m)	Precision ($\overline{CV}_T$):	0.068
Procedure:	Adsorption on Tenax GC, desorption with carbon tetrachloride, GC	Validation Date:	11/25/77

1. Principle of the Method

1.1 A known volume of air is drawn through a glass tube containing Tenax GC to trap biphenyl vapors.

1.2 Biphenyl is desorbed from the Tenax GC with carbon tetrachloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.642-2.35 mg/cu m at an atmospheric temperature of 24.5°C and atmospheric pressure of 760 mm Hg, using a 30-liter sample. This sample size is based on the capacity of the Tenax GC to collect vapors of biphenyl in air at high relative humidity. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method depends on the adsorptive capacity of the Tenax GC. This capacity may vary with the concentrations of biphenyl and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 20 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough occurred after 130 minutes at an average sampling rate of 0.532 liter/minute and relative humidity greater than 84% and temperature of 24°C. The breakthrough test was conducted at an average concentration of 2.49 mg/cu m.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as biphenyl at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.642-2.35 mg/cu m was 0.068. This value corresponds to a 0.07 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 On the average, the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 7.3% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.24 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of micrograms that the tube will hold before overloading. When the amount of biphenyl found on the backup section of the Tenax GC tube exceeds 25% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

6.2 Tenax GC Tubes: Glass tube with both ends unsealed, 6.0-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 35/60 mesh Tenax GC separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 20 mg of Tenax GC, and the

backup section contains 10 mg. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be less than 10 mm of mercury at a flow rate of 0.50 liter per minute. Immediately prior to packing, the empty glass tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. The Tenax GC tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to usage, Tenax GC* is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch to batch differences in production. A quantity of Tenax GC is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Tenax GC is added to the sorbent and mixed, and a vacuum is applied. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C under 25 inches mercury vacuum for four hours.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (1.8 m long x 4-mm I.D. glass) packed with 5% OV-17 on 80/100 mesh Chrom W.

6.5 An electronic integrator or some other suitable method of determining peak areas.

6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.

6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.

6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.

6.10 Stopwatch.

6.11 Manometer.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Acetone, reagent grade.

7.2 Biphenyl, reagent grade.

* Tenax GC is a solid adsorbent manufactured by Enka N.V. (Holland). It is available through many domestic distributors.

7.3 Carbon tetrachloride, reagent grade.

7.4 Hexane, reagent grade.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative Tenax GC tube in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tube. All tubes must be packed with Tenax GC from the same manufacturer's lot.

8.3.2 The smaller section of Tenax GC is used as a backup and should be positioned nearer the sampling pump.

8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tube.

8.3.5 A sample size of 30 liters is recommended. Sample at a flow rate of 0.50 liter/minute or less. Do not sample at a flow rate less than 0.01 liter/minute. Record the sampling time, flow rate, and type of sampling pump used.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The Tenax GC tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank. A minimum of 18 extra Tenax GC tubes should be provided for desorption efficiency determinations.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the Tenax GC tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Tenax GC tube. Remove the glass wool plug and transfer the first (larger) section of Tenax GC to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Tenax GC to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to effect complete transfer of the Tenax GC.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of CCl_4 is pipetted into each sample container. All work with CCl_4 should be performed in a hood because of its high toxicity. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the biphenyl is desorbed.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

50 ml/min (60 psig) nitrogen carrier gas flow
50 ml/min (24 psig) hydrogen gas flow to detector
500 ml/min (50 psig) air flow to detector
225°C injector manifold temperature
250°C detector manifold temperature
135°C column temperature

A retention time of approximately 6 minutes is to be expected for biphenyl under these conditions and using the column recommended in Section 6.4. The carbon tetrachloride will elute from the column before the biphenyl.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn,

taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Tenax GC.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Tenax GC.

8.5.2 Tenax GC equivalent to the amount in the first section of the sampling tube (20 mg) is measured into a 2-ml glass sample container and capped. This Tenax GC must be from the same batch as that used in obtaining the samples. If extra sampling tubes are available, biphenyl may be spiked onto the front section of the tube and then transferred to a 2-ml glass container. A known amount of a hexane solution of biphenyl containing 9.45 mg/ml is injected directly into the Tenax GC with a microliter syringe, and the sample container is capped. The amount injected is equivalent to that present in a 30-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to ensure complete adsorption of the biphenyl onto the Tenax GC. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of the biphenyl-hexane solution into 1.0 ml of carbon tetrachloride with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in micrograms recovered from the tube divided by the weight in micrograms added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (micrograms)}}{\text{Weight added (micrograms)}}$$

The desorption efficiency is dependent on the amount of biphenyl collected on the Tenax GC. Plot the desorption efficiency versus weight of biphenyl found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/1.0 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

9.1 Prepare several stock standard solutions of biphenyl in carbon tetrachloride.

9.2 From the above stock solutions, appropriate aliquots are withdrawn and dilutions are made in carbon tetrachloride. Prepare at least 5 working standards to cover the range of 3.8-113 micrograms/ml. This range is based on a 30-liter sample.

9.3 Prepare a standard calibration curve by plotting concentration of biphenyl in micrograms/ml versus peak area.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on micrograms/1.0 ml carbon tetrachloride and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

micrograms = micrograms sample - micrograms blank

where:

micrograms sample = micrograms found in front section of sample tube
micrograms blank = micrograms found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected micrograms/sample.

$$\text{Corrected micrograms/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of biphenyl in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected micrograms (Section 10.4)}}{\text{Corrected air volume (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

M.W. = molecular weight of biphenyl

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Diphenyl, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S24

November 25, 1977

Substance

Diphenyl (Biphenyl)

Standard

8-hour time-weighted average: 0.2 ppm (1 mg/cu m)

Analytical Method

A known volume of air is drawn through a tube containing 35/60 mesh Tenax GC to trap the biphenyl vapors present. The biphenyl is desorbed from the Tenax GC with carbon tetrachloride, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 0.642-2.35 mg/cu m for a 30-liter sample at 24.5°C and 760 mm Hg atmospheric temperature and pressure.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow can be determined accurately (±5%) at a flow rate of 0.50 liter per minute. A tube (6.0 cm long with a 6-mm O.D. and a 4-mm I.D.), containing two sections of 35/60 mesh Tenax GC separated by a 2-mm portion of urethane foam, is used to collect the samples. The front section of the tube contains 20 mg of Tenax GC, and the backup section contains 10 mg. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Prior to packing, the Tenax GC is prewashed in acetone. NIOSH Method S24 for Diphenyl describes the prewashing procedure.

Sample Size

A sample size of 30 liters is recommended. Sample at a flow rate of 0.5 liter/minute or less. Do not sample at a flow rate less than 0.01 liter/minute.

Sampling Procedure

1. Immediately before sampling, remove the caps from the ends of the tube. All tubes must contain Tenax GC from the same manufacturer's lot.

2 The smaller section of Tenax GC is used as a backup and should be positioned nearer the sampling pump. Air should flow through the larger front section before entering the smaller backup section.

The Tenax GC tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of biphenyl.

3. Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tube.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature, relative humidity, and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump that is used.

5. The Tenax GC tube should be capped individually with plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. From the same lot of tubes used for sample collection, submit one blank Tenax GC tube and an additional blank tube for every ten samples. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this tube as a blank. Information on the batch number of the Tenax GC must be supplied. A minimum of 18 extra Tenax GC tubes should be provided for desorption efficiency determinations. This is necessary, because desorption efficiency may vary among different batches of Tenax GC and different laboratories.

Special Considerations

1. When other compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

2. Due to the high resistance of the Tenax GC tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without first fully recharging the battery.

3. The volume recommended is based on high humidity breakthrough tests. Further reduction in sample volume due to high humidity should not be needed. If condensation of water occurs in the tube, the substance may not be trapped quantitatively.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Capped Tenax GC tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tube.

Reference

Diphenyl, NIOSH Method No. S24.

Backup Data Report No. S24

November 25, 1977

Substance: Diphenyl (Biphenyl)

OSHA Standard: 0.2 ppm (1 mg/cu m)

Chemical Used for Validation: Biphenyl
Matheson, Coleman and Bell

General

The procedure for collection and analysis of air samples containing biphenyl is described in NIOSH Method No. S24. This method consists of collection of the biphenyl on Tenax GC, desorption with carbon tetrachloride, and analysis of the resulting solution by gas chromatography.

This method has been tested for validity for a 30-liter air sample using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) should be less than 25% at the OSHA standard level 95% of the time.

The protocol used for testing this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of biphenyl to represent 30-liter air samples.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

Determine the breakthrough capacity of Tenax GC at high relative humidity.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S24. The results of the desorption efficiency tests are in Table S24-7. Tenax GC, 35/60 mesh, Lot 04901, available through Applied Science Laboratories, Inc. was used in the validation study.

Sampling and Analysis

Test atmospheres of biphenyl were generated using the apparatus described in Attachment A. The apparatus was immersed in a beaker of oil at room temperature in order to maintain a constant temperature throughout the experiment. Biphenyl was generated from the pure solid which has a high vapor pressure. A flow rate of air at 1.9 liters/minute carried the biphenyl vapors into the dilution system described in Attachment B. Appropriate dilution with air was made to obtain samples at 2X, 1X, and 0.5X the OSHA standard levels. The samples were collected using sampling tubes containing 20 mg of Tenax GC in the front adsorbing section and 10 mg in the backup section.

Six samples were collected from each chamber at an average flow rate of 0.50 liter per minute for 60 minutes to obtain 30-liter air samples. Six additional samples were collected at 1X the OSHA standard level and were used for the storage stability tests. The results of the analyses of the samples used for the validation study are presented in Table S24-8. The backup sections of the sampling tubes at the 2X level were analyzed and found to contain less than the limit of detection, which was 0.003 mg/cu m.

Storage Stability

A study was done to assess whether biphenyl would be successfully stored for one week after collection. A second set of six samples at 1X the OSHA standard level (1.24 mg/cu m, as determined by the independent method) was collected at the same time as the samples that were used for validation. The samples were collected for 60 minutes at an average flow rate of 0.50 liter/minute. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results of the analyses are given below in Table S24-1.

Table S24-1

Storage Stability Test

Samples Analyzed Immediately (mg/cu m)	Samples Analyzed After One Week (mg/cu m)
1.182	1.115
1.147	1.080
1.113	1.100
1.172	1.102
1.171	1.089
1.138	1.091
mean 1.154	1.096
std dev 0.026	0.012
CV 0.023	0.011

The criterion for acceptance was that the mean of the six samples stored at room temperature for seven days should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 5%; thus, the storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed at an average relative humidity of 85%. Details of the method of generating atmospheres containing high relative humidities are given in Attachment C. The test atmosphere was generated using the apparatus described in Attachment A. The generation parameters used during breakthrough tests were as follows:

Oil bath: 25°C (room temperature)
Air flow rate: 1.90 liters/minute at 25°C
Dilution air flow rate: 60.5 liters/minute at 25°C

Breakthrough is defined as that time when 5% of the influent concentration appears in the effluent of the front section of sorbent.

Since the concentration of biphenyl in the air samples was too low to monitor directly, it was necessary to measure the amount of biphenyl collected on the front and backup sections of Tenax GC tubes and calculate the breakthrough time. The test for breakthrough was conducted as follows:

Breakthrough was measured by sampling through sampling tubes containing 20 mg of Tenax GC in the front section and 10 mg in the backup section. Single tubes were removed at specified time intervals, and the front and backup sections were analyzed. The data is summarized in Table S24-2.

Table S24-2

Breakthrough Study

Time Removed (minutes)	Sample Volume (liters)	µg Found (Front)	µg Found (Backup)	% back µg / back + front µg
60	31.5	79.0	0.092	0.1
90	48.6	115.9	1.76	1.5
120	64.2	153.8	5.44	3.5
135	71.4	162.6	10.1	6.2

By plotting % biphenyl found back/biphenyl found front vs time, it was found that breakthrough occurred at 130 minutes, at a volume of 74.5 liters. Based on the data obtained, a sample volume should not exceed 50 liters at a concentration level of 2.49 mg/cu m. A 30-liter sample was found to be adequate for sensitivity of the analytical method.

The concentration of biphenyl in the test atmosphere was monitored as described in the Independent Method Section. Two midget bubblers connected in series (each containing 10 ml of methanol) were used to collect samples to monitor the concentration of biphenyl during the test. The samples were collected at an average flow rate of 0.454 liter/minute. The bubblers were changed every 30 minutes during the duration of the breakthrough test. The collected samples were analyzed by uv absorbance at a wavelength of 247.5 nm. The results are presented in Table S24-3.

Table S24-3

Generator Concentration During Breakthrough Study

Time Interval (minutes)	Concentration Generated (mg/cu m)
0-30	2.51
30-60	2.51
60-90	2.50
90-120	2.54
120-150	2.42
mean	2.50

Independent Method

An independent method of measuring the concentration of biphenyl was conducted so that the results obtained from the validated method could be compared. Samples were collected using two midget bubblers connected in series. Each bubbler contained 10 ml of methanol. Three samples at each of 2X, 1X, and 0.5X the OSHA standard levels were collected simultaneously. Different sampling rates at each level were used to obtain samples in the linear range of the calibration curve. The sampling rates used were:

2X	0.183 liter/minute
1X	0.519 liter/minute
0.5X	0.951 liter/minute

After sampling, methanol was added to each bubbler to bring the volume to 10 ml. The samples were analyzed by uv absorbance at a wavelength of 247.5 nm.

A calibration curve was prepared by analyzing known concentrations of biphenyl in methanol and plotting concentration biphenyl vs absorbance. The curve was used to determine the concentration of biphenyl for the independent method. The results of the analyses of the samples used for the independent method are presented in Table S24-4.

Table S24-4
Independent Method

Level	Sample Volume (liters)	µg front bubbler	µg backup bubbler		mg/cu m
2X	10.98	25.3	2.3		2.51
	10.68	19.8	4.2		2.27
	11.22	23.8	1.7		2.27
				mean	2.35
1X	30.54	34.5	1.6		1.182
	31.68	38.0	3.1		1.297
				mean	1.240
0.5X	58.6	36.2	1.4		0.642
	56.6	31.7	1.9		0.594
	56.0	33.1	5.7		0.689
				mean	0.642

Discussion

Preliminary work was conducted to find an appropriate gc column for the analysis of biphenyl. The columns tried are summarized below.

Table S24-5
Preliminary GC Study

Column	Results
5% SE-30 on Chrom W, 1.2-m x 6-mm glass	Poor retention of biphenyl (1 minute at 130°C) and bad solvent tailing
10% FFAP on Chrom W, 2.7-m x 3-mm stainless steel	Good separation, but some solvent tailing (7 minutes at 150°C, 4.5 minutes at 170°C)
Porapak Q, 1.2-m x 3-mm stainless steel	Biphenyl never eluted, even at 200°C for 1 hour
5% OV-17 on Chrom W, 1.8-m x 6-mm glass	Best separation with minimum solvent tailing

From the above results, the 5% OV-17 glass column was selected.

Work was done to determine a suitable collecting sorbent and desorbing solvent for biphenyl. Four microliters of a solution containing 28.25 micrograms/microliter of biphenyl in hexane was used to spike the sorbent. The results of the experiment are presented in Table S24-6.

Table S24-6

Preliminary D.E. Study

Sorbent	Desorbing Solvent	D.E. (%)	Comments
Charcoal 104 (100 mg)	Methanol	0	
	Carbon Disulfide	52	
	Benzene	65	
	CCl_4	2	
	Ethyl Ether	0	
	Acetone	2	
Porapak Q (50 mg)	Methanol	53	
	Carbon Disulfide	104	Porapak Q transparent
	Benzene	98	Porapak Q transparent
	CCl_4	93	
	Ethyl Ether	92	
	Acetone	93	
Tenax GC (35 mg)	Methanol	83	
	Carbon Disulfide	64	
	Benzene	79	
	CCl_4	99	
	Ethyl Ether	93	
	Acetone	92	
XAD-2 (30 mg)	CCl_4	94	
	Acetone	89	

From the above results, Tenax GC was selected as the sorbent, and CCl_4 the desorbing solvent. XAD-2 resin and Porapak Q were not selected, because they require an extensive clean-up procedure before use.

Work on butyl mercaptan showed that different lots of Porapak Q may affect method recoveries. Impurities which are left from the manufacturing process of Porapak Q may react with the analyte or interfere with the GC analysis. Although no impurities were found to be present in the Tenax GC used, a clean-up step was deemed necessary as a precautionary measure.

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2.

The precision of the analytical method was assessed using the data in Table S24-7. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.019.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S24-8 and the results obtained from breakthrough tests and storage stability tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from test atmospheres is 0.045. To obtain a measure of the accuracy of the method, the mean value of the concentration found by analysis at each level was compared with the value for the concentration taken.

The average recovery (concentration found divided by concentration taken) for all three levels was 92.7%. The value for the taken concentration was obtained as described under the Independent Method Section. The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test, described above.

The total Coefficient of Variation ($\overline{CV}_T$) is 0.068.

Table S24-7

Data Sheet: Diphenyl

Analysis

Level	0.5X			1X			2X	
µg taken	µg found	D.E.	µg taken	µg found	D.E.	µg taken	µg found	D.E.
18.90	18.47	0.977	37.8	37.9	1.003	75.5	73.7	0.976
18.90	17.93	0.949	37.8	37.8	1.000	75.5	75.5	1.000
18.90	18.67	0.988	37.8	39.3	1.040	75.5	74.8	0.991
18.90	17.76	0.940	37.8	37.7	0.997	75.5	73.2	0.970
18.90	18.23	0.965	37.8	36.8	0.974	75.5	76.1	1.008
18.90	18.62	0.985	37.8	37.9	1.003	75.5	75.2	0.996
		6			6			6
mean		0.967			1.003			0.990
std dev		0.020			0.021			0.015
CV_1		0.021			0.021			0.015

$\overline{CV}_1$ 0.019

$\overline{CV}_{A+\overline{DE}}$ 0.021

Table S24-8

Data Sheet: Diphenyl

Sampling and Analysis

Test Level	Found				Taken	Percent Recovery
	µg	Corr µg*	Liters	mg/cu m**	mg/cu m	
0.5X	19.40	20.06	32.3	0.621	0.642	
	19.83	20.51	32.1	0.639	0.642	
	17.71	18.31	32.5	0.563	0.642	
	16.81	17.38	32.2	0.540	0.642	
	17.79	18.40	32.0	0.575	0.642	
	17.36	17.95	32.3	0.556	0.642	
			n = 6			
			mean	0.582		90.7
			std dev	0.039		
			CV_2	0.067		
1X	37.7	37.7	31.9	1.182	1.240	
	36.7	36.7	32.0	1.147	1.240	
	35.5	35.5	31.9	1.113	1.240	
	37.4	37.4	31.9	1.172	1.240	
	37.7	37.7	32.2	1.171	1.240	
	36.4	36.4	32.0	1.138	1.240	
			n = 6			
			mean	1.154		93.1
			std dev	0.026		
			CV_2	0.023		
2X	72.0	72.0	31.5	2.286	2.350	
	68.8	68.8	31.9	2.157	2.350	
	69.0	69.0	32.0	2.156	2.350	
	70.5	70.5	31.8	2.217	2.350	
	67.1	67.1	31.3	2.144	2.350	
	73.2	73.2	31.6	2.316	2.350	
			n = 6			
			mean	2.213		94.2
			std dev	0.074		
$\overline{CV}_2$ 0.045			CV_2	0.033		

* The corr µg was calculated using an average desorption efficiency of 0.967 at the 0.5X level and an average desorption efficiency of 1.00 at the 1X and 2X levels.

** All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference 2.

References

1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

Attachment A

Vapor Generation System

Test atmospheres of organic vapors can be generated with an apparatus described in Reference No. 1, which describes a method for measuring liquid vapor pressure.

The vapor generator was adapted from the apparatus described in Reference No. 1. A schematic diagram of this vapor generator is shown in Figures S24-1 and S24-2. The vapor generator consists of two sections--a generating section (Figure S24-1) and a diluting section (Figure S24-2) which are connected by a ground glass joint.

The generating section (Figure S24-1) 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. Air 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 air determine the actual amount of vapor generated. Increasing either the air flow or the bath temperature, increases the amount of vapor generated.

The diluting section (Figure S24-2) 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.

The equations given in Reference No. 1 can be used to determine the approximate vapor concentration in the saturated air 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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1. Physical Methods of Chemistry, Part V, A. Weissberger and B. W. Rossiter, eds., (John Wiley & Sons, 1971), 61-66.

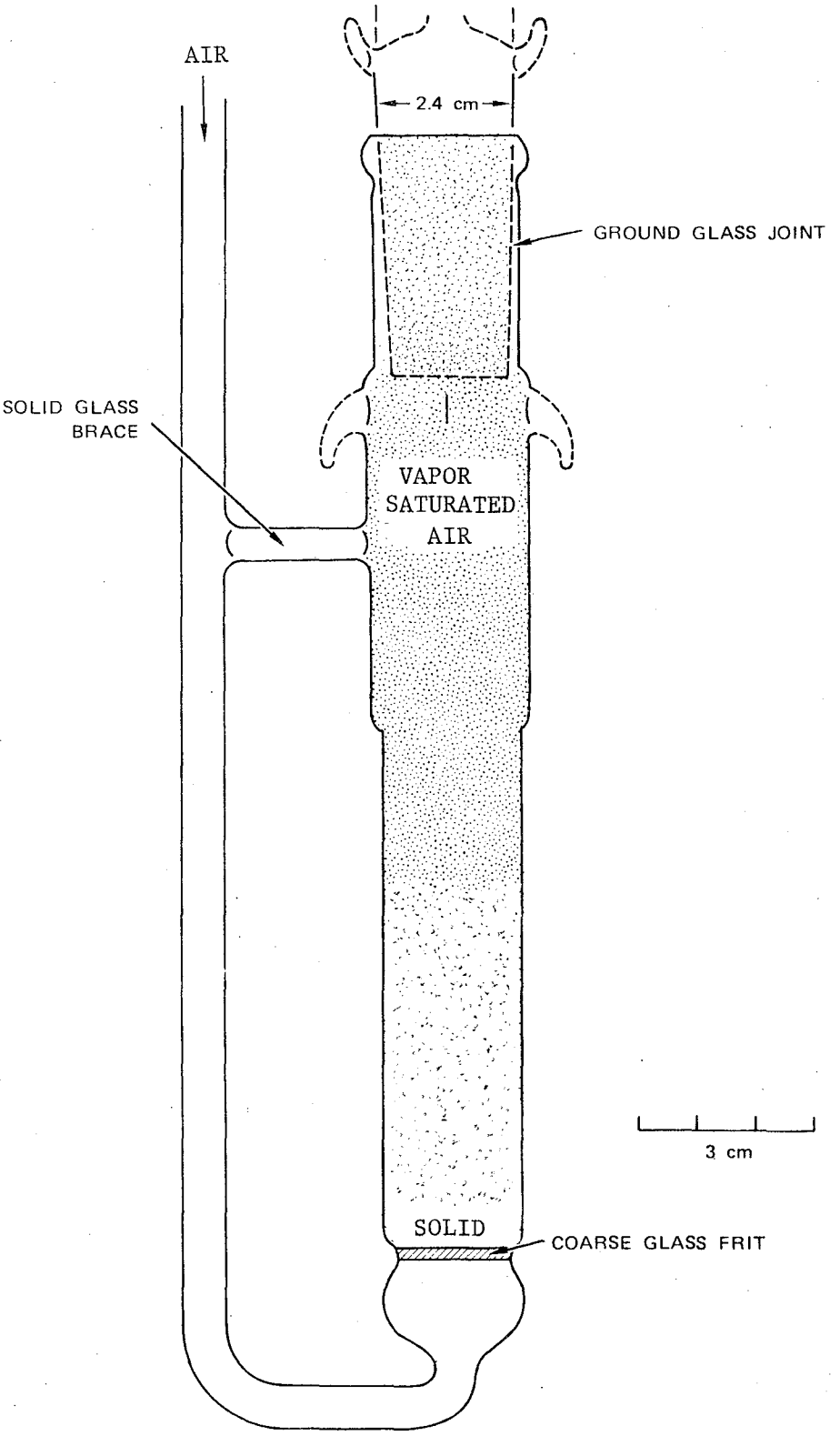


FIGURE S24-A1 VAPOR GENERATOR (generating section)

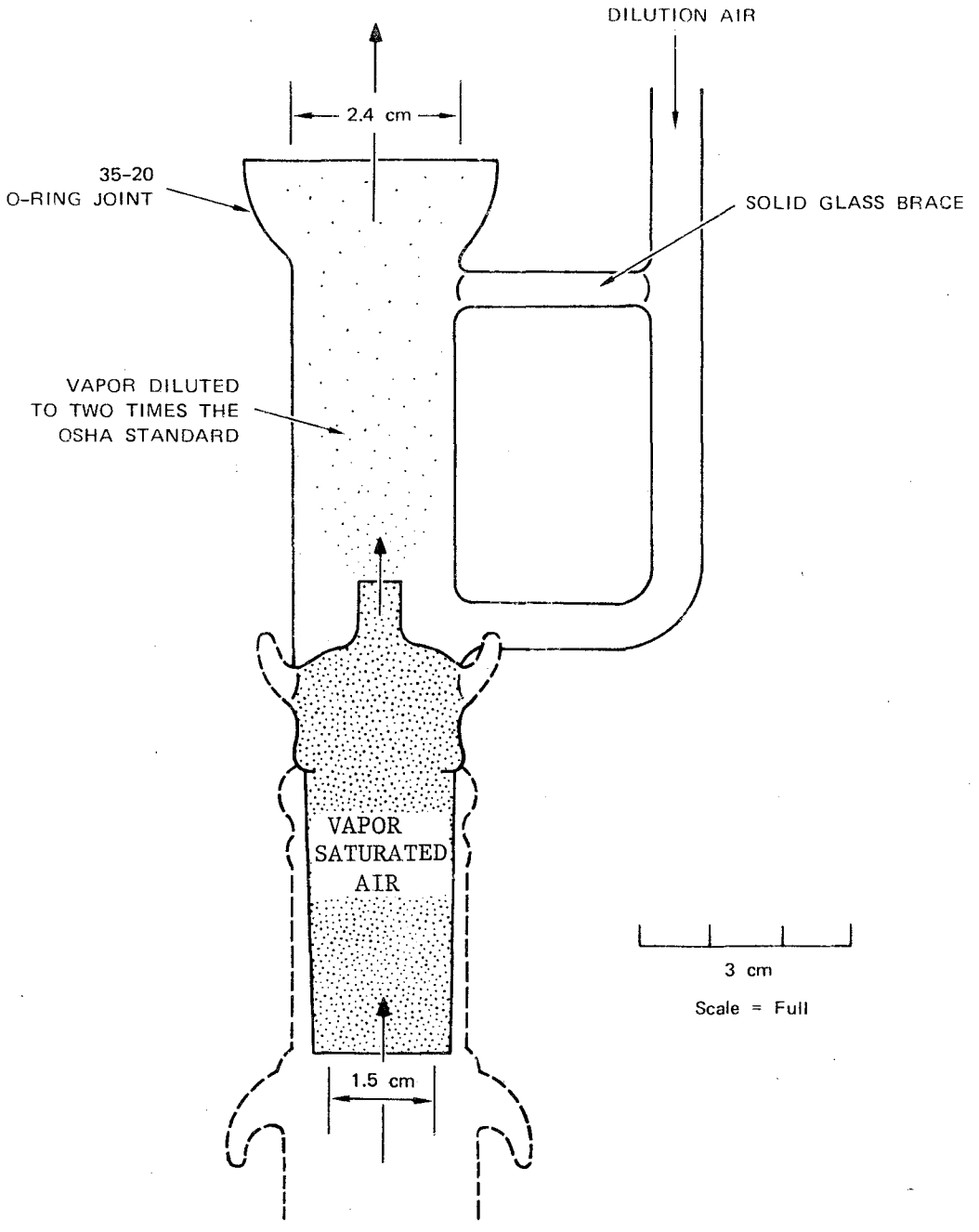


FIGURE S24-A2 VAPOR GENERATOR (diluting section)

Attachment B

Generation of Test Atmospheres

The system for generating and collecting samples of vapor, inorganic/organic particulate, dusts, and fumes 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. A schematic of the generation system and associated components is presented in Figure 1.

The generation system is large enough to be used for polydispersed aerosols as well as for gases and vapors. The primary dilution chamber is 48 inches by 4 inches and may handle air flows up to 400 liters/minute. The large volume dilution chamber is important for several reasons. Even at high air flow rates, the velocity of particles is low to allow complete solvent evaporation in the generation of aerosols. The air velocity is also low enough to avoid impaction on the walls while great enough to prevent particle diffusion to the walls. For these same reasons, the sample rationing system is only 1 inch in diameter and handles a flow of only 52 liters/minute. Gravitational settling is avoided by maintaining a sufficient air velocity.

The sampling cones for the three chambers are 6-inch I.D. at the base (point of sample collection) and narrow to 1-inch I.D. at the point of attachment to the sample rationing system. A constant total air flow of 26 liters/minute through each cone causes a gradual reduction in aerosol velocity toward the point of sample collection. The air velocity at the collection point is 2.4 cm/second.

All portions of the generation system that come in contact with the test atmosphere are constructed of stainless steel or Teflon to avoid any contamination problems. Sections of the generation system at which dilution air is added are constructed such that the incoming air forms a "high-velocity sheath" around the air/analyte mixture that is to be diluted. This sheath serves two functions. The dilution air sheath becomes increasingly less coherent and stable as it moves downstream of its point of entrance and hence is turbulently mixed with air/analyte test atmosphere. At the point of entrance of the dilution air stream, a Venturi effect accelerates the air/analyte mixture to a high velocity. The dilution air sheath also prevents interaction of the accelerated air/analyte stream with the walls of the chamber, thus eliminating a large source of aerosol loss by impaction.

The system being used to generate the initial concentrations of vapor, gas, or particulate is interfaced with the dilution apparatus at the primary dilution chamber. The output of the generator is diluted with the appropriate amount of air to obtain a concentration 2X the OSHA standard. Of the total amount of material generated at the 2X level, a flow of 52 liters/minute enters the rationing system. Under control of a vacuum exhaust orifice, material at the 2X level enters the first sampling chamber at a rate of 26 liters/minute. Downstream of the entrance to the first sampling chamber, dilution air is added (via a critical orifice) at a rate of 26 liters/minute. Thus the flow of material at the 2X level that did not enter the first sampling chamber

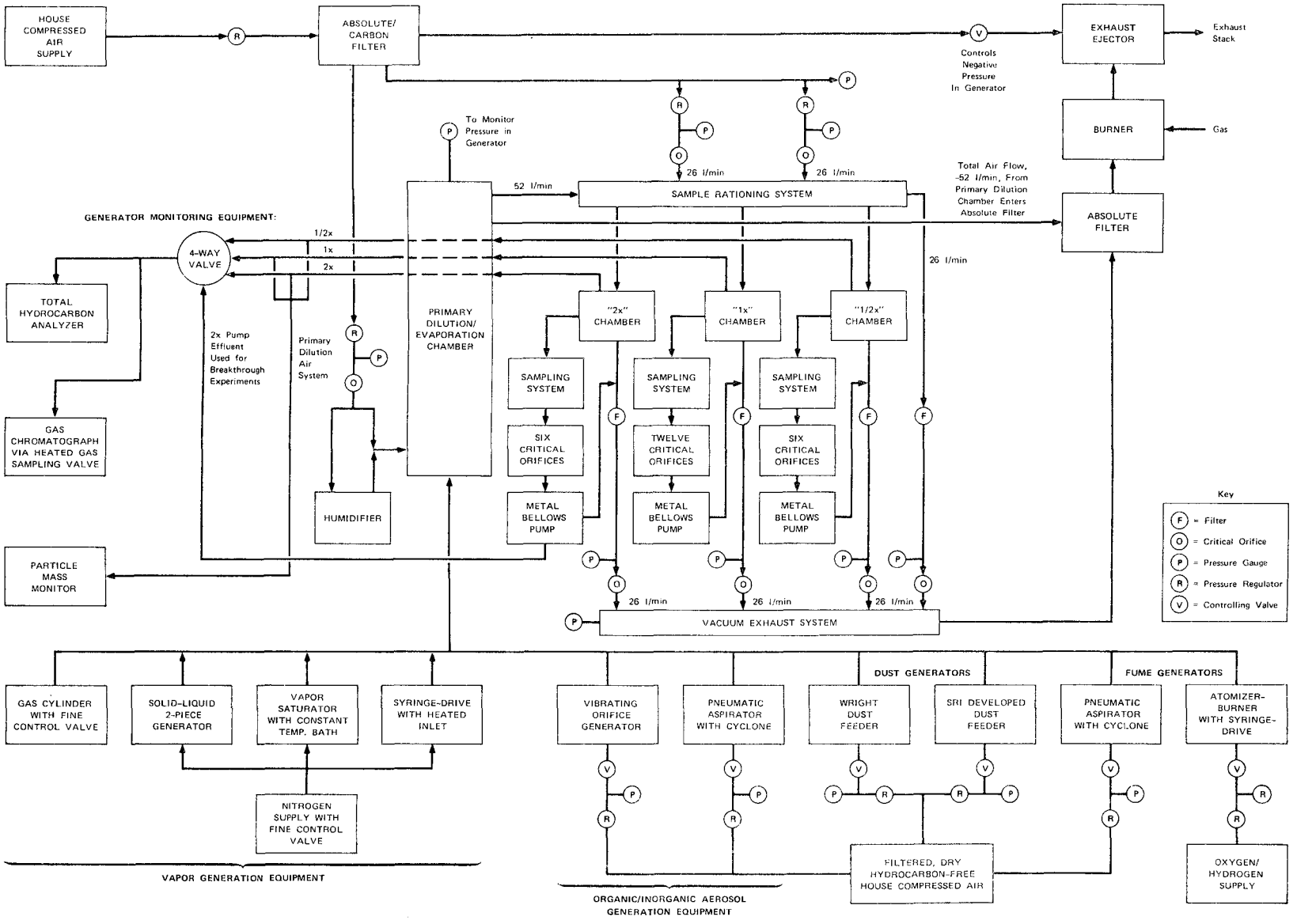


FIGURE S24-B1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

S24-B2

(26 liters/minute) is diluted with air at a flow rate of 26 liters/minute to a final concentration of 1X the OSHA standard level. Analyte at the 1X level then enters the second sampling chamber at a rate of 26 liters/minute. The remaining flow, 26 liters/minute is diluted again with air at 26 liters/minute to achieve 0.5X the OSHA standard level. The analyte/air mixture at the 0.5X level is drawn into the third sampling chamber at 26 liters/minute. The remaining material in the rationing system not drawn into the sampling chambers is removed at a rate of 26 liters/minute by the fourth critical orifice in the vacuum exhaust system. This removal of test atmosphere volumes and addition of measured volumes of air thus achieves serial dilutions to 1X and 0.5X the OSHA standard level.

The dilution ratios from chamber to chamber can also be varied by simply changing the amount of dilution air that is added. This is particularly advantageous in generating aerosols, where wall deposition of particles in the rationing system can be offset by changing the rate of addition of dilution air.

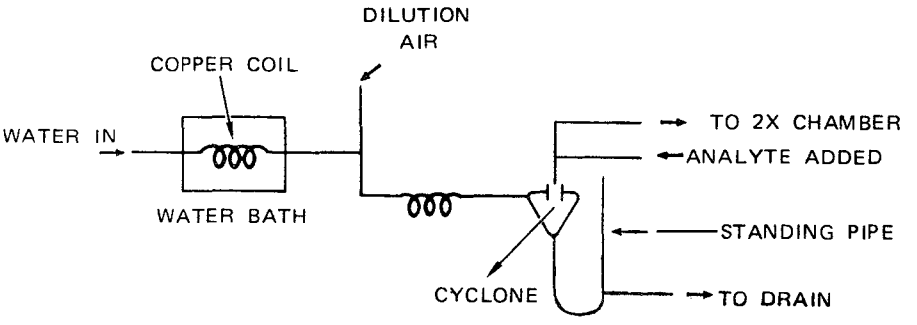
The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected simultaneously. A metal bellows vacuum pump is used for sampling from each chamber. Separate critical flow orifices are used for each sample. Air taken from the chamber during sampling is returned via the sampling pump exhaust line to the chamber outlet line, thus preserving the proper air flows during the time of sampling. The sampling rate therefore does not affect the concentration of material in any of the chambers.

The entire system is maintained at 1-inch water vacuum to prevent toxic materials from escaping into the laboratory. All exhaust air streams (from the vacuum exhaust system and excess from the primary dilution chamber) are fed into a combustion chamber where all toxic materials present are burned before entering the atmosphere.

Attachment C

Generation of Known Humidity Test Atmospheres

A diagram of the apparatus used for generating high humidity atmospheres is shown below.



A regulated flow of tap water at approximately 15°C flowed through a copper coil contained in the thermostated water bath. After emerging from the water bath it entered a 5-foot length of 5/16-inch Tygon tubing. The dilution air was introduced into this same tubing and became water saturated at the temperature of the bath. This water-air mixture passed into a cyclone, where excess water was removed from the air stream and drained from the bottom of the cyclone. The U-shaped tube and standing pipe provide a water seal at the bottom of the cyclone to prevent loss of air by this route. The humid air left through the top of the cyclone. A controlled flow of the analyte entered the air stream at the outlet of the cyclone at a rate such that the 2X concentration was obtained.

The temperature of the water bath was kept 1°C lower than the temperature of the room. Thus, the air was saturated with water vapor at the lower temperature and reached a relative humidity of less than 100% as it warmed to room temperature after leaving the cyclone.

The value for the relative humidity of the air in the sampling chamber is found by consulting relative humidity tables.

Picric acid

Analyte:	Picric acid	Method No:	S228
Matrix:	Air	Range:	0.036 - 0.189 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.082
Procedure:	Filter collection, extraction with 70% aqueous methanol, HPLC	Validation Date:	11/25/77

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the picric acid aerosol present. This method is not applicable for sampling environments where significant picric acid vapor may be present.

1.2 The filter is transferred to a jar and extracted with 70% aqueous methanol.

1.3 An aliquot of the sample is injected into a high performance liquid chromatograph (HPLC) equipped with a variable wavelength UV detector set at 360 nm.

1.4 The area of the resulting sample peak is used as a measure of analyte concentration by comparison with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.036 - 0.189 mg/cu m at an atmospheric temperature and pressure of 22°C and 772 mm Hg, using a 180-liter sample.

2.2 The method may be extended to higher values by further dilution of the sample solution. The detection limit of the analytical method is estimated to be at least 10 ng per ml.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any other compound which has the same retention time as the analyte at the operating conditions

described in this method is an interference. Retention time data based on a single set of conditions cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.036 - 0.189 mg/cu m was 0.082. This value corresponds to a 0.008 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedure are found in Reference 11.2.

4.2 A collection efficiency of at least 99% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the filters was 99.3%. In addition, the samples were found to be stable when stored for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

5.2 This sampling method is applicable for particulate picric acid only; in operations where significant vapor may also be present, this method will not apply.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 Filter. The filter unit consists of a mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter, supported by a cellulose backup pad, and a 37-mm, three-piece filter holder held together by tape or a shrinkable band.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate is needed. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Barometer.

6.1.5 Stopwatch.

6.2 High pressure liquid chromatograph equipped with a detector capable of UV detection at 360 nm.

6.3 Column (30-cm x 3.9-mm I.D. stainless steel) packed with μBondapak C_{18} or equivalent.

6.4 Syringe. Twenty-μl, for HPLC injection.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes. One hundred-microliter and other convenient sizes for making standard solutions.

6.7 Ointment jars. Use squat form with Teflon film gaskets and screw cap.

6.8 Volumetric flasks. Twenty-five milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Picric acid, reagent grade.

7.2 Distilled water.

7.3 Methanol in distilled water, 70%. Prepare by diluting 700 ml of methanol to 1000 ml with distilled water. This solution is used for sample extraction and also as the mobile phase for the HPLC analysis, but should be degassed prior to such use.

7.4 Picric acid stock solution, 1.8 mg/ml. Dissolve 0.18g of picric acid in 100 ml of 70% methanol.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter holder in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.3.2 Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.

8.3.4 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 With each batch of samples, submit one filter which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples.

8.3.10 The filter holders should be shipped in a suitable container designed to prevent damage in transit.

8.3.11 A bulk sample of the suspected material should be submitted to the laboratory in a glass container lined with a Teflon cap. Label of the bulk sample should match air samples for identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the cellulose membrane filter from the holder with the aid of appropriate tweezers and transfer filter to the 2-oz. ointment jar.

2. Add 5 ml of 70% methanol to the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

8.4.2 Analysis by high pressure liquid chromatography. The mobile phase is 70% aqueous methanol. The typical operating conditions for the liquid chromatograph are:

1. 1.0 ml/min solvent flow rate

2. Ambient column temperature

3. 2250 psi system pressure

4. 360 nm UV detection wavelength

5. Capacity ratio: 2.2

8.4.3 Injection. The first step in the analysis is the injection of the sample into the liquid chromatograph. A 20 µl-sample aliquot is recommended for this analysis. The sample may be injected either by using an appropriate syringe or by filling a fixed volume sample loop provided that reproducibility requirements are satisfied. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the

recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter with 5 ml of 70% methanol and analyzed as described in Section 8.4.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 180-liter sample at the selected level was used to determine the analytical method recovery. A stock solution containing 0.975 milligrams of picric acid per milliliter of 70% aqueous methanol was prepared. Ten, 20 and 40-microliter aliquots of the solution were added to the cellulose membrane filters and air-dried to produce samples equivalent to 180-liter collections at 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand overnight. A parallel blank filter was also prepared except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered - Blank (µg)}}{\text{Weight (µg) added}}$$

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

9.1 From the stock standard solution, prepare at least 6 working standards to cover the concentration range of 9-36 µg/5 ml. Transfer 25 to 100 µl-aliquots of the stock standard into 25-ml volumetric flasks and dilute to volume with 70% methanol.

9.2 This series of standards is analyzed under the same HPLC conditions and during the same time period as the unknown samples. It is convenient to express concentration of standards in µg/5 ml 70% methanol, because samples are extracted in this amount of 70% methanol. Curves are established by plotting concentrations in micrograms per 5.0 ml versus peak area.

NOTE: To minimize effect of variations in LC conditions and detector response due to sample cell conditions, frequent standardization should be practiced.

10. Calculations

10.1 Read the concentration, in µg/5 ml, corresponding to the peak area from the standard curve. No volume corrections for sample aliquots analyzed are needed, because the standard curve is based on µg per 5.0 ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D. C., Order No. 017-033-00231-2.

11.2 S228 Backup Data Report for Picric acid, prepared under NIOSH Contract No. 210-76-0123, November 25, 1977.

Sampling Data Sheet No. S228

November 25, 1977

Substance

Picric acid

Standard

8-hour time-weighted average: 0.1 mg/cu m

Analytical Method

A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the picric acid particulate present. The sample filters are extracted with 70% aqueous methanol and the solution is analyzed by high pressure liquid chromatography using a variable wavelength UV detector set at 360 nm. The method has been validated over a concentration range of 0.036 - 0.189 mg/cu m at 22°C and 772 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The following equipment is needed for sampling picric acid particulate: a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at a flow rate of 1.5 liters per minute; a 37-mm, three piece filter holder held together by tape or shrinkable band; a 37-mm diameter, 0.8 micrometer mixed cellulose ester membrane filter (MCEF) supported by a cellulose backup pad.

Sample Size

A sampling period of two hours is recommended. Sample at a flow rate of 1.5 liters per minute.

Sampling Procedure

1. Assemble the filter in the three-piece filter holder and close firmly to insure that the center ring seals the edge of the filter. The MCEF is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

2. Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

3. Air being sampled should not be passed through any hose or tubing before entering the filter holder.

4. A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

5. Turn the pump on and begin sample collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.

6. Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

7. After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and outlet.

8. Carefully record sample identity and all relevant sample data.

9. With each batch of samples, submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples.

Special Considerations

Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. This sampling method is applicable for particulate picric acid only; in operations where significant vapor may also be present, this method will not apply.

Bulk Sample

A bulk sample of the suspected material should be submitted to the laboratory in a glass container lined with a Teflon cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

The filter holders should be shipped in a suitable container designed to prevent damage in transit.

Reference

Picric acid, NIOSH Method No. S228.

Backup Data Report No. S228
November 25, 1977

Substance: Picric acid

OSHA Standard: 0.1 mg/cu m

Chemical Used for Validation: Picric acid crystals, Fisher Scientific Co.

General Considerations

The method for picric acid has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be $100 \pm 10\%$ and $\overline{CV}_T$ must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for picric acid consisted of the following experimental studies:

- Development of a high pressure liquid chromatographic (HPLC) method for the analysis of picric acid,
- Analysis of a total of eighteen analytical samples (six samples at each of three test levels for a 180-liter sample) prepared by adding known amounts of picric acid to 37-mm Type AA Millipore filters, 0.8 micrometer pore size,
- Analysis of a set of eighteen samples (six samples at each of the three test levels) collected from dynamically generated test atmospheres at 0.5, 1 and 2X the OSHA standard for a 180-liter sample,
- Determination of the collection efficiency on mixed cellulose ester membrane filters,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The HPLC method tested experimentally and documented in this report has passed all the requirements of this program.

Development of Analytical Method

Initial experiments conducted with picric acid were aimed at determining the vapor content of samples collected at the OSHA standard test level. On the basis of extrapolating available data, the vapor pressure of picric acid has been estimated to be 0.00047 mm Hg at 40°C (Reference 3). Several experiments were carried out in order to confirm whether picric acid exists as a vapor at significant levels or whether picric acid vaporization losses can occur during sampling. Each of these experiments is outlined below. All analyses were done by HPLC on a μBondapak C_{18} column.

In the first set of experiments picric acid samples were generated using the Aerosol/Generation/Dilution Sampling System described in Attachment A. In each generation experiment the physical layout of the sampling train was such that particulate picric acid would be collected by a front filter, a front bubbler or a front impinger, while any vapor would be trapped in a backup collector (bubbler, impinger or Tenax-GC sorbent tube). The impingers contained 15 ml of water or methanol for sample collection, while the bubblers contained 10 ml of ethylene glycol. The impingers which contained methanol were diluted to 25 ml prior to analysis. In all subsequent cases no dilution was made in an attempt to increase sensitivity. A minimum of three samples of each sampling unit were collected and analyzed. However, no appreciable amount of picric acid was detected from any impinger or bubbler solution, whether positioned as a front or a backup collector, while the filters consistently collected between 0.1 and 0.15 mg of picric acid per cubic meter of air at the 1S level indicating that the collection efficiency of the bubblers and impingers was too poor to allow any conclusions to be reached from these experiments. Similarly, no picric acid vapor was detected on any sorbent tubes positioned as backup collectors.

The possibility of vaporization losses was further examined by collecting six filter samples, storing these samples for seven days and comparing the results to six one-day-old samples. No loss of picric acid was observed. Furthurmore, no picric acid was detected on the cellulose backup pads stored with the filters.

In another experiment, six samples were collected on filters at the 2S level. An additional 90 liters of room air was then pulled through three of these samples. All filters were extracted in 5 ml of 70% aqueous methanol and analyzed by HPLC. The results are summarized in Table S228-1. Only a 3% difference was observed between the two sets of samples.

Due to the inefficiency of the impingers and bubblers tested, as described above, a further experiment was conducted using the vapor generation system described in Attachment B. An attempt was made to generate picric acid vapor by passing a stream of nitrogen at 2.4 liters per minute over picric acid crystals in a generation tower. Samples of the

Table S228-1

Data Sheet: Picric acid

Determination of Volatilization During Sampling

	µg	Liters		mg/cu m
No room air sampled	52.8	185.0		0.2854
	50.0	185.1		0.2701
	50.5	185.2		0.2727
			mean	0.2761
			CV_2	0.02966
90% room air sampled	50.4	185.3		0.2720
	49.4	185.1		0.2669
	48.5	184.0		0.2636
			mean	0.2675
			CV_2	0.01582

main line concentration were collected at 1 liter per minute for 120 minutes on 100 mg of 35/60 mesh Tenax-GC. The desorption efficiency from 100 mg of Tenax-GC spiked with 18 µg of picric acid was shown to be at least 80%. Desorption was done in 2 ml of 70% aqueous methanol. Once again, no picric acid vapor was detected. Based on a detection limit of 10 ng/ml for this experiment, approximately 0.2% of the OSHA standard concentration could exist as a vapor.

The above data indicates that picric acid is a particulate at the test concentrations of interest. It is also noted, however, that at higher temperatures where picric acid may exist as a vapor, this method would not be functional and an alternate collection method should be used.

Principle of the Method

The method validated for the analysis of picric acid in air is based on collection on a mixed cellulose ester membrane filter, recovery from the filter by 70% methanol extraction and analysis by high pressure liquid chromatography.

Analysis

The details of the equipment and instruments used for the analysis and general approach used are described in Attachment C.

A detailed description of the procedure for analysis, the preparation of analytical samples for the determination of recovery, and the preparation of calibration standards are given in NIOSH Method No. S228 (Reference 4).

The reliability of the analytical method was tested based on the analysis of eighteen filter samples. The analytical samples were prepared by spiking 37-mm Type AA Millipore filters with known aliquots of picric acid in an aqueous 70% methanol solution. The aliquots added contained respectively 9.75, 19.5 and 39 micrograms of picric acid representing the equivalent of a 180-liter air sample at 0.5, 1 and 2X the OSHA standard.

After overnight storage, each filter was placed in a 2-oz. ointment jar and treated with 5 milliliters of 70% aqueous methanol. The jars were sealed with a screw cap and Teflon film gasket. The data for the full set of eighteen samples analyzed by reversed phase chromatography is given in Table S228-2.

Sampling and Analysis

Particulate picric acid was generated using the basic Aerosol Generation/Dilution/Sampling System described in detail in Attachment A.

Table S228-2

Data Sheet: Picric acid

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
9.75	9.83	1.008	19.50	18.05	0.926	39.0	36.9	0.946
9.75	10.28	1.054	19.50	19.15	0.982	39.0	35.5	0.910
9.75	9.97	1.023	19.50	19.40	0.995	39.0	38.8	0.995
9.75	10.51	1.078	19.50	19.80	1.015	39.0	37.8	0.969
9.75	10.24	1.050	19.50	20.45	1.049	39.0	34.4	0.882
9.75	9.74	0.999	19.50	20.20	1.036	39.0	37.5	0.962
n =		6			6			6
mean		1.035			1.000			0.944
std dev		0.0303			0.0441			0.0414
CV_1		0.02931			0.0441			0.0438

$\overline{CV}_1$ 0.0397

$\overline{CV}_{A+AMR}$ 0.0429

The Environmental Research Corporation Fluid Atomization Aerosol Generator was used for these studies.

Test atmospheres at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of picric acid containing 0.7 grams of picric acid per liter of water into a dry, solvent-free airstream flow. The atomizer air flow was 9 liters per minute; aerosol from the Collison type atomizer was diluted with 150 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a concentration 2X the OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain concentrations at 1 and 0.5X the OSHA standard levels. All six samples at the three test levels were collected simultaneously at 1.5 liters per minute for 120 minutes (180 liters). The eighteen samples were analyzed as described in NIOSH Method No. S228 and the data are summarized in Table S228-3.

Particle Size Distribution

Studies were also conducted to determine the particle size distribution of the picric acid aerosol produced in the test chamber. The method used was sampling with an Andersen cascade impactor (Particle Fractionation Personnel Sampler) and determination of the amount of picric acid deposited at each stage by extraction with 70% methanol and analysis by HPLC.

The data obtained by HPLC analysis of the picric acid collected at each stage of the cascade impactor are tabulated below. The effective cutoff aerodynamic diameter in micrometers for each stage are based on manufacturer's quotations which has been determined at a flow rate of 1.4 liters per minute. Under the actual experimental conditions of this test, the flow rate through the impactor was 1.48 liters per minute. The cumulative percent is based on cumulating from the last stage of the impactor.

Stage	Particle Size Range Cut-off Diameter (µm)	µg Picric Acid Found	% Total Particulate	Cumulative %
1	4.7 and up	0.133	1.0	100.0
2	<4.7 - 3.3	0.090	0.7	99.0
3	<3.3 - 2.1	0.015	0.1	98.3
4	<2.1 - 0.65	0.315	2.4	98.2
Backup Filter	<0.65	12.60	95.8	95.8
	TOTAL	13.15		

Table S228-3

Data Sheet: Picric acid
Sampling and Analysis

Test Level	Found			Taken	
	µg	Liters	mg/cu m	mg/cu m$^{\Delta}$	Recovery
0.5S	5.52	172.2	0.0321	0.0360	
	5.65	171.7	0.0329	0.0360	
	3.42	165.7	0.02064*	0.0360	
	5.84	172.8	0.0338	0.0360	
	6.20	172.8	0.0359	0.0360	
	5.65	169.7	0.0333	0.0360	
		n = 5			
		mean	0.0336		0.933
		std dev	0.001428		
		CV_2	0.0425		
1S	17.35	182.9	0.0949	0.1077	
	17.35	183.1	0.0948	0.1077	
	18.40	182.3	0.1009	0.1077	
	18.10	182.3	0.0993	0.1077	
	18.20	183.4	0.0992	0.1077	
	18.60	182.9	0.1017	0.1077	
		n = 6			
		mean	0.0985		0.914
		std dev	0.002959		
		CV_2	0.0300		
2S	25.55	176.1	0.1451	0.1893	
	30.3	168.5	0.1798	0.1893	
	30.4	176.9	0.1718	0.1893	
	30.8	176.9	0.1741	0.1893	
	31.4	175.2	0.1792	0.1893	
	33.6	173.5	0.1937	0.1893	
		n = 6			0.919
		mean	0.1740		
		std dev	0.01606		
		CV_2	0.0923		
		$\overline{CV_2}$	0.0623		

$^{\Delta}$ Based on the UV analysis of six samples at the OSHA standard. See Table S228-6 for more detailed information.

* This value excluded from statistical analysis on the basis of Grubb's outlier test as described in Reference 2.

Storage Stability

Studies were done to assess the stability of picric acid samples collected on mixed cellulose ester membrane filters and stored at ambient conditions for seven days. For these studies, a set of twelve samples was collected from a dynamically generated test atmosphere. Six of these samples were analyzed as described in Section 8.4 of NIOSH Method No. S228 after overnight storage. The other six samples were stored for seven days and analyzed similarly. The data for these samples are shown in Table S228-4 and indicate that the picric acid samples are stable upon storage. The average recovery was 96% for the one-day-old samples vs. 90.7% for the seven-day-old samples.

Collection Efficiency

The collection efficiency of 37-mm Type AA Millipore filters for picric acid was determined by collecting six filter samples at a test concentration of 0.1502 mg/cu m for a 180-liter sample. The physical layout of the filter series (front and backup) used for all samples was such that the two filters were physically separated from each other and only the backup filter was supported by a cellulose backup pad. The overall average collection efficiency found was 99.2% at the test concentration studied as indicated by the data summarized in Table S228-5.

Independent Method of Verifying Generator Concentration

The concentration of picric acid particulate produced by the generation/dilution system was verified by an independent collection and analysis. Samples were collected at 1.5 liters per minute on 37-mm Type AA Millipore filters with subsequent extraction in 5 ml of 70% aqueous methanol. The resulting solutions were analyzed by UV spectrophotometry at a wavelength of 360 nm using a Perkin-Elmer/Coleman UV Spectrophotometer. Six samples for this analysis were collected at the OSHA standard level simultaneously with the eighteen samples listed in Table S228-3, and are presented in Table S228-6 together with the summarized data from the validated method. Similarly, six samples at 2X the OSHA standard were collected simultaneously with the twelve 1S level samples in Table S228-4. These data are summarized in Table S228-7. In both cases, the mean value for the collected samples analyzed by UV spectrophotometry is used as the "taken" concentration at the appropriate OSHA standard level. The "taken" values at the remaining levels were calculated based on measured dilution ratios of 0.191, 0.569 and 1.00 for generation levels of 0.5, 1 and 2X the OSHA standard. Note that the mg/cu m of picric acid "taken" and "found" at the 0.5S level, as reported in Table S228-3, is less than one half times the OSHA standard ±25%. This was due to a greater than fourfold dilution at the 0.5S line relative to the 2S (main) line. However, the recovery and precision are satisfactory and meet the requirements for validation as stated in Reference 1.

Table S228-4

Data Sheet: Picric acid

Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found			Taken	
	µg	Liters	mg/cu m	mg/cu m*	Recovery
1S	21.95	181.8	0.1207	0.1217	
	20.55	182.0	0.1129	0.1217	
	21.25	181.2	0.1173	0.1217	
	20.80	181.2	0.1148	0.1217	
	21.55	182.3	0.1182	0.1217	
	Sample Lost	181.8	-	0.1217	
		mean	0.1168		0.960
		CV_2	0.02591		

Expt. B: Samples Stored 7 Days

1S	20.15	181.8	0.1108	0.1217	
	19.55	176.4	0.1108	0.1217	
	20.35	181.8	0.1119	0.1217	
	20.55	180.2	0.1140	0.1217	
	18.75	179.9	0.1042	0.1217	
	20.25	182.6	0.1109	0.1217	
		mean	0.1104		0.907
		CV_2	0.02982		

* Based on the UV analysis of six samples at 2X the OSHA standard level. See Table S228-7 for detailed information.

Table S228-5

Data Sheet: Picric acid

Collection Efficiency of Picric acid
on 37-mm Type AA Millipore Filters

µg Found			
Front	Backup	Total	% Collected in Front
26.30	0.1900	26.49	99.3
25.60	0.2200	25.82	99.1
25.00	0.2050	25.20	99.2
25.45	0.0920	25.54	99.6
26.00	0.1600	26.16	99.4
27.35	0.320	27.67	98.8

Average Collection Efficiency....99.2

Table S228-6

Data Sheet: Picric acid

Comparison of Validated Method and Independent Method for One-Day-Old Samples

Found by HPLC	----------Found by UV Analysis----------		
mg/cu m[1]	µg	Liters	mg/cu m
0.0949	19.80	182.9	0.1083
0.0948	18.60	177.5	0.1048
0.1009	19.25	182.9	0.1052
0.0993	19.40	181.2	0.1071
0.0992	20.55	181.0	0.1135
0.1017	19.70	183.7	0.1072

n = 6		n = 6	
mean	0.0985	mean	0.1077
std dev	0.002959	std dev	0.00314
CV_2	0.0300	CV_2	0.02915

(1) Refer to Table S228-3 for detailed information.

Table S228-7

Data Sheet: Picric acid

Comparison of Validated Method and Independent Method for Storage Stability Samples

--Found by HPLC--	---------- Found by UV Analysis ----------			
Level 1S mg/cu m[1]	µg	Liters	2S mg/cu m	1S mg/cu m[2]
0.1207	37.0	175.0	0.2114	0.1203
0.1129	37.4	167.5	0.2233	0.1271
0.1173	37.6	175.8	0.2139	0.1217
0.1148	37.0	175.8	0.2105	0.1198
0.1182	Sample Lost	-	-	-
Sample Lost	36.6	174.2	0.2101	0.1195

n = 5		n = 5	
mean	0.1168	mean	0.1217
std dev	0.00303	std dev	0.00315
CV_2	0.02591	CV_2	0.02585

(1) Refer to Table S228-4 for detailed information.

(2) Calculated by multiplying the mg/cu m found at the 2S level by the measured dilution ratio of 0.569.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S228-2 and S228-3.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1 and 2X the OSHA standard for generated samples. The data (Table S228-3) gave a chi squared value of 5.87, indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$\overline{CV}_1 = 0.0397$ $\overline{CV}_2 = 0.0623$ $\overline{CV}_T = 0.0815$

The accuracy of the method was determined by comparison of the average value found by analysis of each set of 6 samples at each of the three test levels with the taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 92.2%.

----- mg/cu m -----

Test Level	Taken	Found	Agreement (Found ÷ Taken)
0.5S	0.0360	0.0336	0.933
1S	0.1077	0.0985	0.914
2S	0.1893	0.1740	0.919
		Average =	0.922

The difference between the taken and found concentrations is considered to result from experimental uncertainities in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, U.S. Government.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D. C., Order No. 017-033-00231-2.

3. Kirk - Othmer Encyclopedia of Chemical Technology. J. Wiley & Sons Publishers, Inc., New York 8, (1965).

4. Picric acid, NIOSH Method No. S228, prepared under NIOSH Contract No. 210-76-0123, with validation date 11/25/77.

ATTACHMENT A

DILUTION AND SAMPLING SYSTEM FOR AEROSOL TEST ATMOSPHERES

The dilution and sampling system used to produce the appropriate aerosol test atmospheres is shown schematically in Figure S228-A-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. These branches are designated as A, B, and C in Figure S228-A-1. The dilution and sampling branches A and C are identical and each is equipped with a sampling manifold with six sample ports. The dilution and sampling branch B, on the other hand, is equipped with a sampling manifold with 14 sample ports. Figures S228-A-2 and S228-A-3 show these dilution and sampling branches 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 main line, 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.

Aerosol dilution occurs in the Teflon venturi-shaped inserts shown in Figures S228-A-2 and S228-A-3. 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 as described in the section on air supply below.

Isokinetic sampling probes, six for branches A and C, and 14 for branch B, 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. There is a luer fitting on each sample port to mate with the filter cassette. Sample flow rate 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 S228-A-1).

As is indicated in Figure S228-A-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. For the dilution/sampling branches A and C, there are seven outwardly flowing streams in each branch--one stream is that which flows through the orifice mentioned above (flow rate Q_T) and the other six are the sample streams (total flow rate Q_S). For the dilution/sampling branch B, the flowing streams consist of one which flows through a critical orifice downstream from the sample probes (flow rate Q_T) and fourteen from the sample streams (total flow rate Q_S). There are two inflowing streams--the dilution air stream (flow rate Q_D) and the aerosol stream entering from the main line (flow rate Q_A). The dilution ratio, R, in

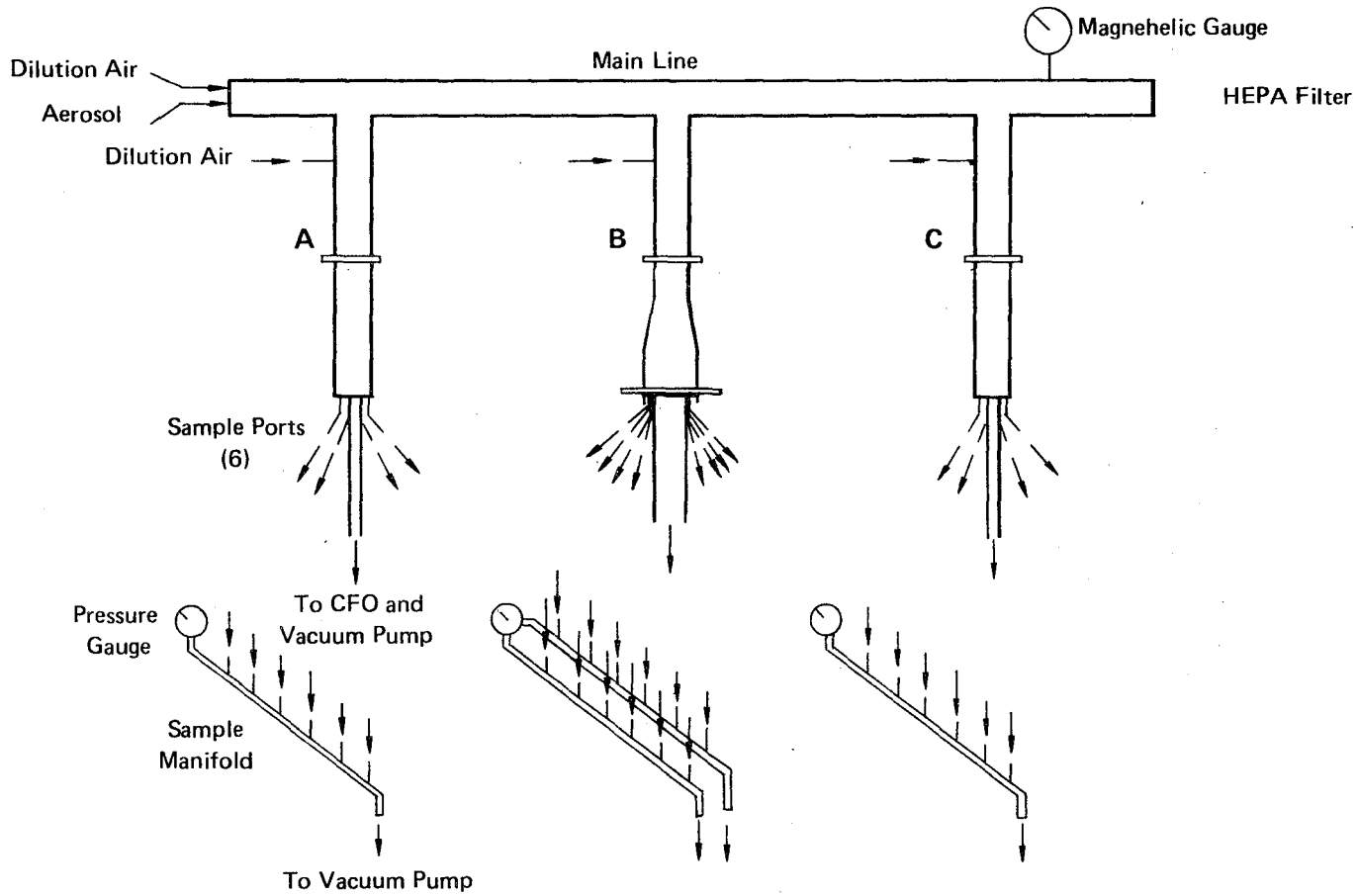


Figure S228-A-1 **AEROSOL DILUTION AND SAMPLING SYSTEM**

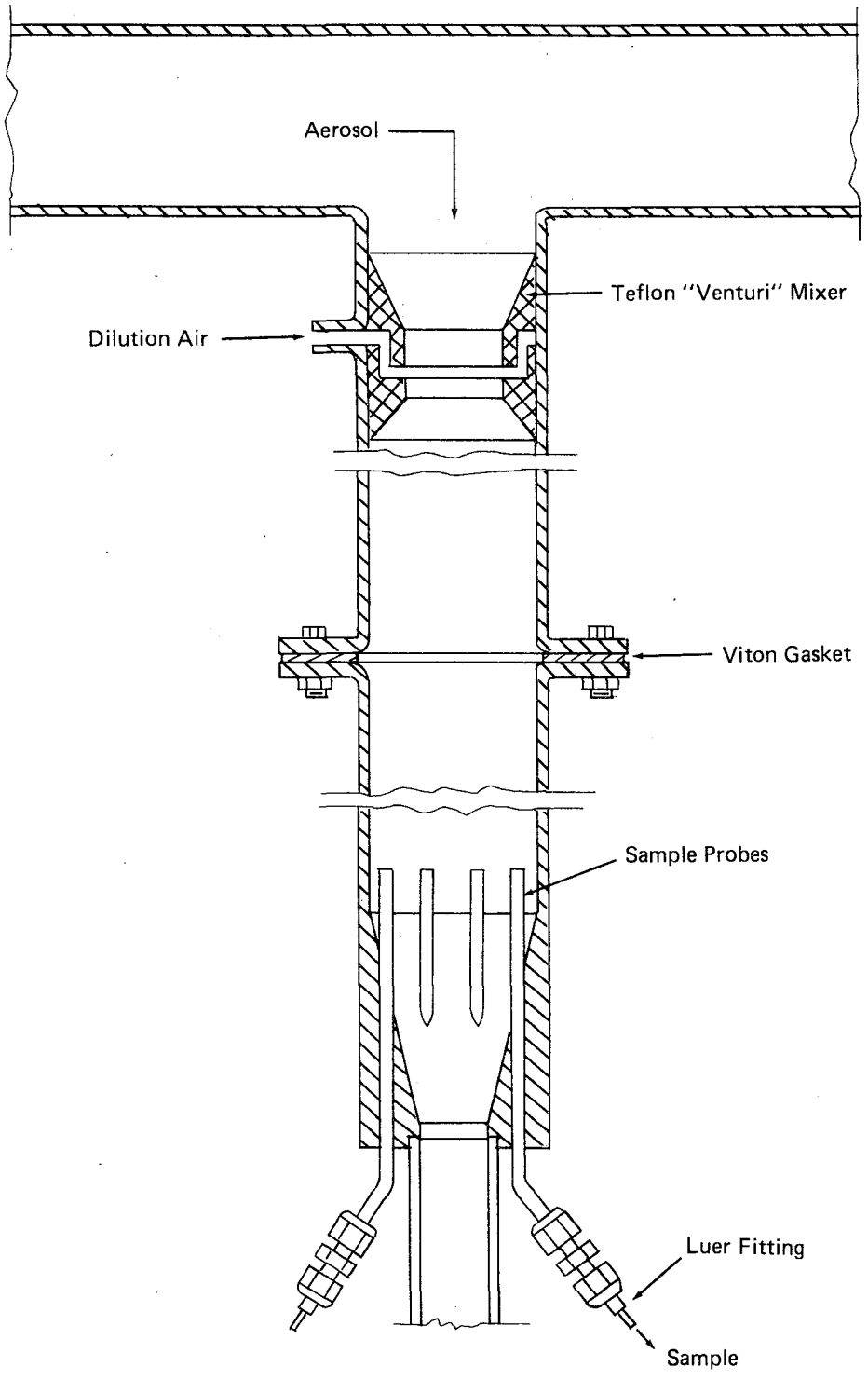


Figure S228-A-2

CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION (BRANCHES A AND C)

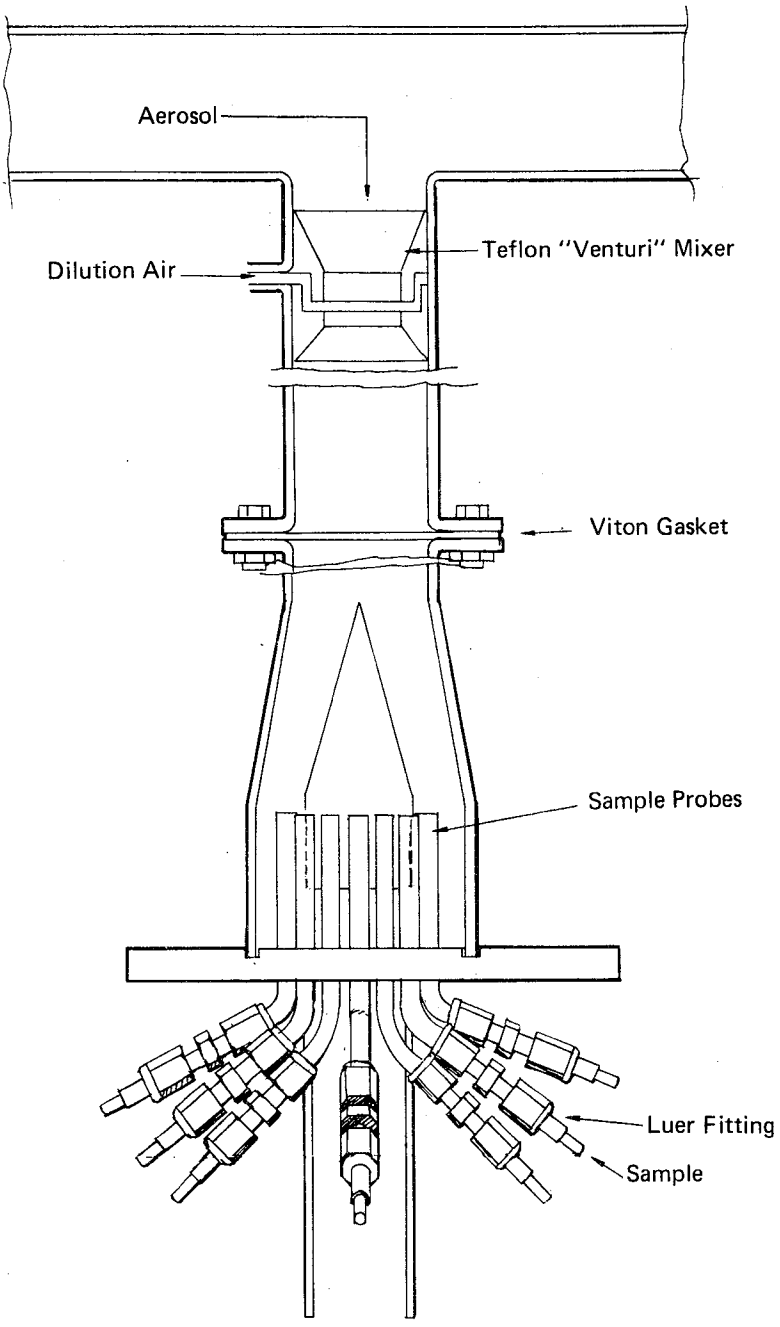


Figure S228-A-3

CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION (BRANCH B)

each branch is given by the correlation:

$$R = \frac{Q_A}{Q_A + Q_D}$$

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 flow rates, 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. No measurable differences (within 1%) in the hydrocarbon concentration were found among the six or fourteen sample ports at any of the three sampling branches. The dilution ratios are rechecked periodically and the typical values are shown in the following section.

The main line flow rate is about 130 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.

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 collections 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).

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 carried out in the trial runs.

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 twenty-four 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 flow rate:	130 liters per minute
Sampling rate:	1.5 liters per minute
Flow rate through dilution/ sampling branch (approximate):	70 liters per minute
Dilution air flow rate (approximate):	
2X OSHA standard, Branch C	0
1X OSHA standard, Branch B	36
0.5X OSHA standard, Branch A	53
Dilution ratios measured with hydrocarbon analyzer (Branch C: Branch B: Branch A)	1.00: 0.54: 0.22*

* The dilution ratio is influenced by system pressure and is experimentally determined periodically.

ATTACHMENT B

VAPOR GENERATION

Vapor Saturation Technique

This technique is used under two circumstances: 1) when a vapor is to be generated from a solid substance of sufficiently high vapor pressure, or 2) when a liquid substance has such a low OSHA standard that generation by syringe injection is impossible. In both cases the vapor saturation tower in Figure S228-B-1 is used. For the case of solids, the material is placed inside the tower. In the case of liquids, the substance is coated onto some type of solid support, such as chromosorb P, and the coated support is placed within the saturation tower. Air or nitrogen is then passed through the tower at a controlled rate and temperature to produce the vapor concentration desired.

Calculation of Main Line Concentration

The simplest way to calculate the Main Line concentration is to weigh the vapor saturation tower before and after generation. The difference, in mg, divided by the amount of air passing through the Main Line during generation, will yield the concentration in mg/cu m. The amount of air passing through the Main Line is calculated by multiplying the elapsed time times the calibrated flow rate. This method is most reliable when differences of more than 100 mg are measured.

Often the substances generated by the vapor saturation method have OSHA standards which are too low to calibrate with the procedure given above. In these cases an alternative sampling and analytical method is used to provide a check on the vapor concentration produced.

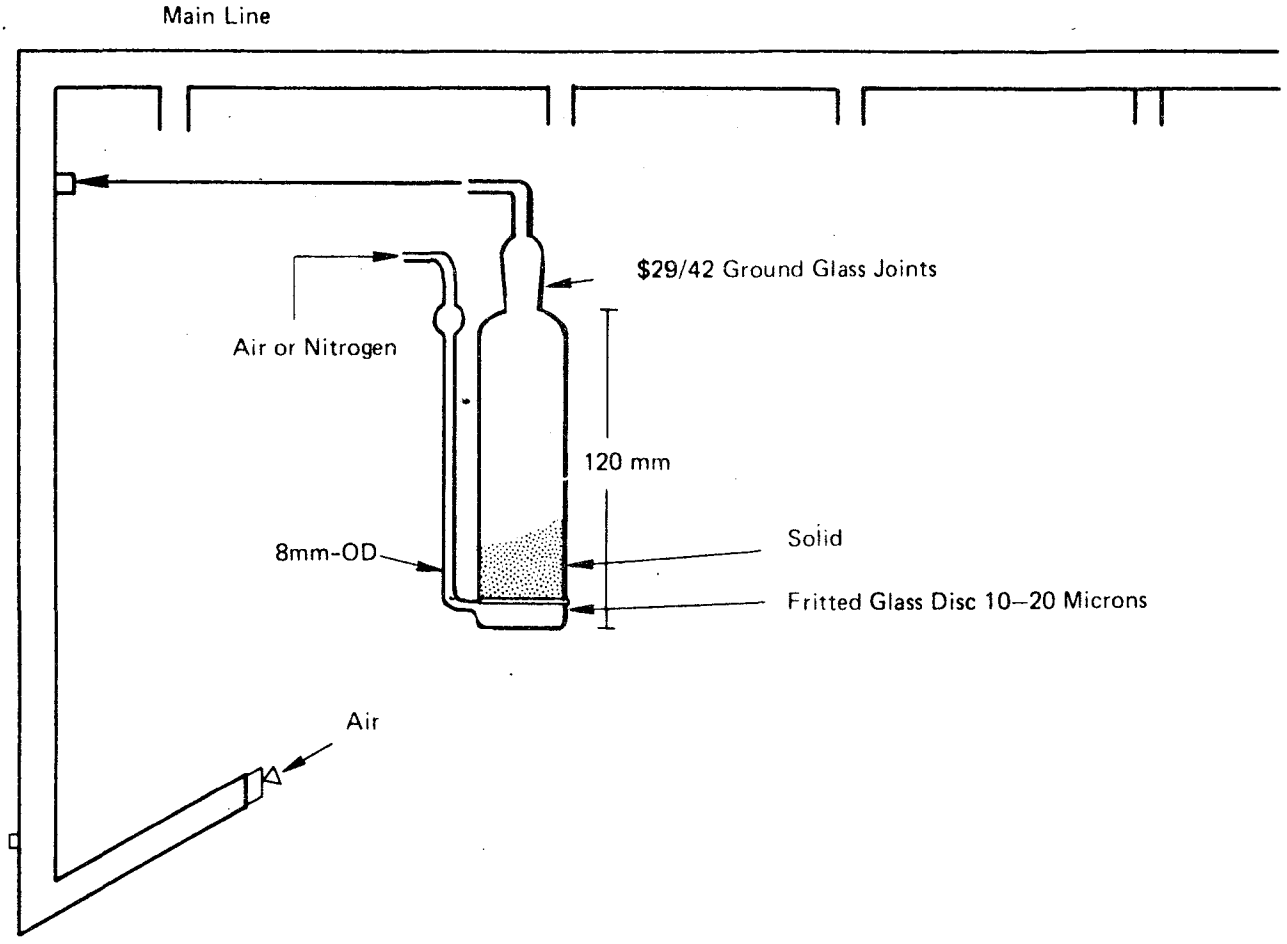


Figure S228-B-1 **VAPOR GENERATOR FOR SOLIDS**

ATTACHMENT C

LIQUID CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the high pressure liquid chromatography (HPLC) method consists of the following:

1. Waters Associates Inc. Model 6000 A Solvent Delivery System,

2. Schoeffel Instrument Corp. SF 770 Monitor Spectroflow and GM 770 Monochromator,

3. Rheodyne Model 7120 Syringe Loading Sample Injector,

4. Spectra Physics System I Computing Integrator.

The Waters Associates Model 6000 A solvent delivery system is especially designed and optimized for liquid chromatography. Constant pulseless flow is achieved with a pair of specially driven positive displacement pumping heads. Flow control is achieved by digital dials in 0.1 ml/min intervals with a range of 0.1 to 9.9 ml/min. Pressurization from 0 to 6000 psig is standard.

A Schoeffel Model SF 770 detection system is used. The SF 770 is a double-beam variable wavelength UV-VIS detector capable of monitoring from below 200 nm to 630 nm. Absorbance ranges of 0.01 to 2.0 are available as well as 1-100% T.

Sample injection is achieved with the Rheodyne Model 7120 syringe loading sample injector. Sample loops, available in 10-100 µl sizes, are filled manually by syringe.

Two injection techniques can be used with this sampling device; either full or partial filling of the sample loop. In this program the sample loop is filled completely to improve reproducibility. The sample loop is rinsed with carrier solvent between injections in order to prevent cross contamination and insure that maximum reproducibility is maintained. This is vitally important since the external (absolute area) standard method is used.

All peak area measurements are done with the System I computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System I also has the capability to calculate sample concentration directly once the calibration factor has been determined.

Pentachlorophenol

Analyte:	Pentachlorophenol	Method No.:	S297
Matrix:	Air	Range:	0.265-1.130 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.072
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date:	12/23/77

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 15 ml of ethylene glycol to collect pentachlorophenol.

1.2 The filter and bubbler are disconnected. The filter is removed from the filter holder and added to the bubbler flask.

1.3 Just before analysis, ten milliliters of methanol is added to the bubbler flask. The resulting sample is analyzed by high performance liquid chromatography using a UV detector set at 254 nm.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.2654-1.131 mg/cu m at an atmospheric temperature of 24°C and pressure of 761 mm Hg, using 180-liter samples.

2.2 The upper limit of the range of the method is dependent on the capacity and collection efficiency of the sampling system. The method may be extended to higher values than those tested by dilution of the sample solution.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as pentachlorophenol at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 0.2654-1.131 mg/cu m was 0.0721. This value corresponds to a standard deviation of 0.036 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.

4.2 A collection efficiency of at least 99% was determined for the collection media (filter and bubbler in series), thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method. The average recovery from the filters was 100.9%. The average recovery from samples that were stored eight days was 95.3%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

6.1 Filter Units. The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer, supported by a stainless steel screen on a 37-mm three-piece filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.

6.2 Flexible Teflon or polyethylene tubing to connect the holder to the bubbler.

6.3 A glass midget bubbler containing 15 ml of ethylene glycol.

6.4 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined within ±5% is used. The sampling pump is protected from splashover or solvent condensation by a second empty bubbler positioned between the exit arm of the first bubbler and the pump.

6.5 Barometer.

6.6 Thermometer.

6.7 High performance liquid chromatograph capable of UV detection at a wavelength of 254 nm and a sample injection valve with a 20-microliter external sample loop.

6.8 Column (30-cm x 3.9-mm I.D. stainless steel) packed with μBondapak C_{18}. The porous packing material consists of silica particles with a bonded coating of C_{18} organo-silane. This packing can be obtained from Waters Associates, Milford, Massachusetts.

6.9 An electronic integrator or some other suitable method for measuring peak areas.

6.10 Tweezers.

6.11 Microliter syringes, 50 and 100-microliter.

6.12 Volumetric flasks, convenient sizes for preparing standard solutions.

6.13 Pipets, convenient sizes for preparing standard solutions and 10 and 15-ml pipets for measuring the extraction medium.

6.14 Teflon tubing (15-cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 Pentachlorophenol.

7.2 Dowicide EC-7 (purified pentachlorophenol).

7.3 Ethylene glycol.

7.4 Methanol, distilled in glass.

7.5 Isopropanol.

7.6 Water, deionized and distilled.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter holder, bubbler and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter holder and close firmly. The filter is backed up by a stainless steel screen. Secure the filter holder together with tape or shrinkable band.

8.3.2 Pipet 15 ml of ethylene glycol into each midget bubbler, and mark the liquid level. Be sure that the bubbler frit is completely immersed in the ethylene glycol.

8.3.3 Remove the filter holder plugs and attach the outlet of the filter holder to the inlet arm of the midget bubbler using a short piece of flexible polyethylene or Teflon tubing. Connect the outlet arm of the midget bubbler to a second empty bubbler and then to the personal sampling pump, using short pieces of flexible tubing. The bubblers must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.

8.3.5 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known to within $\pm$5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. Sampling should be terminated when the rotameter cannot be readjusted.

8.3.7 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.8 After sampling, disconnect the filter and bubblers. Remove first the bubbler stem, and remove the filter from the filter holder with clean tweezers and add it to the bubbler. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of pentachlorophenol from the filter by vaporization might occur. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The splashover trap should have the inlet and outlet of the bubbler stem sealed in a similar manner. The standard taper joint of the bubblers should be taped securely to prevent leakage during shipping.

8.3.9 With each batch or partial batch of ten samples submit one bubbler containing ethylene glycol and a blank filter from the same lot of filters used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

8.3.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.3.11 Bulk Sample. A bulk sample of the suspected material should be submitted to the laboratory in a glass container closed by a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

8.4 Analysis of Samples

8.4.1 If the sample volume is less than 15 ml, add ethylene glycol until the volume reaches the 15-ml mark. If the sample volume is more than 15 ml, determine the volume and make an appropriate volume correction in the calculations indicated in Section 10.1.

8.4.2 Add 10 ml of methanol to each sample just before analysis and mix the solution gently but thoroughly.

8.4.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 2300 psi
Flow Rate: 1.6 ml/min
Mobile Phase: 60% methanol/40% water (V/V)
Detector: UV photometer at 254 nm
Capacity Ratio: 1.8

8.4.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 20-microliter sample loop. Flush this loop thoroughly with solvent (300 microliters), then fill the loop with sample solution and inject.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The filter is then immediately placed into 15 ml of ethylene glycol. Prior to analysis, as described in Section 8.4, 10 ml of methanol is added.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 180-liter sample at the selected level was used to determine the analytical method recovery. A stock solution containing 10.00 milligrams of pentachlorophenol per milliliter of isopropanol was prepared. Aliquots of 4.5, 9 and 18 microliters were added to the cellulose membrane filters and air-dried to produce samples equivalent to 180-liter collections at 0.5, 1 and 2X the OSHA standard level. The analytical samples were then placed in 15 ml of ethylene glycol and allowed to stand overnight. A parallel blank filter was also prepared except that no sample was added to it. Just prior to analysis, as described in Section 8.4, 10 ml of methanol was added.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered - Blank (µg)}}{\text{Weight (µg) added}}$$

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.25 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/25 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the UV detector response.

9.1 Prepare a 10 mg/ml pentachlorophenol stock standard solution by dissolving 100 mg pentachlorophenol in isopropanol and diluting to 10 ml in a volumetric flask.

9.2 From the above stock solution, appropriate aliquots are withdrawn and added to a mixture of 15 ml ethylene glycol and 10 ml methanol. Prepare at least five working standards to cover the range of 22.5-270 µg/25 ml. This range is based on a 180-liter sample. Analyze samples as per Section 8.4.

9.3 Prepare a standard calibration curve by plotting concentration of pentachlorophenol in µg/25 ml versus peak area.

10. Calculations

10.1 Read the weight, in µg/25 ml, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on µg/25 ml of ethylene glycol/methanol and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = µg found in sample solution

μg blank = µg found in blank solution

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 For personal sampling pumps with rotameters only, the following volume correction should be made:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of pentachlorophenol in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3) x 1000 (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Pentachlorophenol, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S297
December 23, 1977

Substance

Pentachlorophenol

Standard

8-hour time-weighted average: 0.5 mg/cu m - skin

Analytical Method

A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 15 ml of ethylene glycol to collect pentachlorophenol aerosols and vapors. The filter and bubbler are disconnected, and the filter is removed from the holder and added to the bubbler flask. Pentachlorophenol is separated and analyzed by high pressure liquid chromatography using a μBondapak C_{18} column and a UV detector set at 254 nm. The method has been validated over the range of 0.265-1.130 mg/cu m for a 180-liter sample at 24°C and 761 mm Hg atmospheric temperature and pressure.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow rate can be determined accurately (±5%) at 1.5 liters per minute, a 37-mm three-piece filter holder held together by tape or shrinkable band, and a 37-mm diameter, 0.8 micrometer cellulose ester membrane filter, connected in series with a midget bubbler using flexible Teflon or polyethylene tubing. Rubber tubing must not be used or low results will be obtained. The filter is supported by a stainless steel screen. It is of importance that the screen be used rather than a backup pad, as pentachlorophenol vapors may be partially retained by the pad and again low results obtained. The sampling pump may be protected from splashover by a trap which is a second bubbler inserted between the exit arm of the first bubbler and the pump. Teflon tubing (15-cm long x 7-mm I.D.) or Teflon plugs are needed for sealing the inlet and outlet of the bubbler stems before shipping.

Sample Size

A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

Sampling Procedure

1. Assemble the filter in the three-piece filter holder and close firmly. Secure the holder together with tape or a shrinkable

band. Pipet 15 ml of the collection medium (ethylene glycol) into the first bubbler. Be sure that the frit is completely immersed in the ethylene glycol. Mark the liquid level.

2. Connect the outlet arm of this bubbler to the inlet of the trap which may be a second empty bubbler. Connect the outlet of the trap to the pump's inlet. Liquid collected in the trap must never be returned to the first bubbler.

3. Remove the filter holder plugs and attach the outlet of the holder to the inlet arm of the midget bubbler using a short piece of polyethylene or Teflon tubing. The bubbler and trap must be maintained in a vertical position during sampling.

4. Air being sampled should not pass through any hose or tubing before entering the filter holder.

5. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

6. After sampling, disconnect the filter and bubbler. Remove the bubbler stem, and remove the filter from the filter holder with clean tweezers and add it to the bubbler. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of pentachlorophenol from the filter by vaporization may occur.

7. Carefully record the sample identity and all relevant sampling data such as sample flow rate and collection time.

8. With each batch of ten samples submit one midget bubbler containing 15 ml of ethylene glycol and a blank filter from the same lot of filters used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

Special Considerations

1. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should

be transmitted with the sample.

2. If a significant amount of pentachlorophenol is found by the analyst in the trap or if less than 7 ml of solution remains in the bubbler, the sample should be considered invalid.

Bulk Sample

A bulk sample of the suspected material should be submitted to the laboratory in a glass container closed with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

Reference

Pentachlorophenol, NIOSH Method No. S297.

Backup Data Report No. S297

December 23, 1977

Substance:	Pentachlorophenol
OSHA Standard:	0.5 mg/cu m - skin
Chemical Used for Validation:	Pentachlorophenol - 99%, Aldrich Chemical Co. Dowicide EC-7 antimicrobial (purified pentachlorophenol), Dow Chemical Co.

General Considerations

The method for pentachlorophenol has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100± 10% and $\overline{CV}_T$ must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for pentachlorophenol consisted of the following experimental studies:

- Development of a high performance liquid chromatographic (HPLC) method for the analysis of pentachlorophenol.
- Analysis of a total of 18 analytical samples (6 each at 0.5, 1 and 2X the OSHA standard) prepared by adding the appropriate amounts of pentachlorophenol, 99% to 37-mm Type AA Millipore filters, 0.8 micrometer pore size to represent 180 liters air samples.
- Analysis of a set of 18 samples (six samples at each of the three test levels) collected from dynamically generated test atmospheres of Dowicide EC-7 at 0.5, 1 and 2X the OSHA standard for a 180-liter sample.
- Determination of the collection efficiency on mixed cellulose ester membrane filters, connected in series to a backup bubbler.
- Testing of the storage stability of six collected samples.
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The HPLC method tested experimentally and documented in this report has passed all the requirements of this program.

Development of Collection Methodology

Initial experiments conducted with pentachlorophenol were aimed at determining the vapor content of samples collected at the OSHA standard test level. The vapor pressure of pentachlorophenol was reported to be 0.00011 mm Hg at 20°C according to available data (Reference 3). This corresponds to a concentration of 1.58 mg/cu m under equilibrium conditions. Experiments were then initiated to determine the vapor content of the pentachlorophenol atmospheres generated. All generations were done with Dowicide-EC-7 purified pentachlorophenol. (Its pentachlorophenol concentration was determined by HPLC to be 94.7%).

The Aerosol Generation/Dilution/Sampling System described in Attachments A and B was used. In each generation experiment a cellulose ester membrane filter or an impinger was connected in series to a backup bubbler or impinger. The bubblers and impingers contained 15 ml of ethylene glycol. Ten ml of methanol was added to them just prior to the HPLC analysis. The filters were placed in jars and extracted in 15 ml ethylene glycol to which 10 ml of methanol was added just before analysis. In these preliminary experiments, therefore, filters, bubblers, and impingers were analyzed separately. It was discovered at this time that connecting tubing of rubber could not be used as lower recoveries resulted. Only Teflon or polyethylene tubing is recommended. Also, recovery in samples collected without a front filter was poor compared to the filter/bubbler collections. With two impingers in series, total recovery was 45.5% of the filter/bubbler value while with the impinger/bubbler configuration, recovery was 56.2% of the filter/bubbler value. In general, the amount of pentachlorophenol recovered from a bubbler which was connected to a front filter was 30% of the total sample, indicating the existence of a significant level of vapor.

In another experiment, six samples were collected on filters at 2X the OSHA standard. An additional 180 liters of room air was then pulled through three of these samples. All filters were desorbed and analyzed by the HPLC method described in NIOSH Method No. S297. The results are summarized in Table S297-1. Recovery from the filters through which air had been drawn was only 74.8% of the control filters, indicating possible vaporization during sampling.

In contrast, another experiment in which three samples collected from a generated atmosphere were stored in sealed holders for one week, no loss was noted over three that were analyzed after one day. However, in view of the losses of pentachlorophenol observed when air was drawn through loaded filters, all subsequent work on validation of a method for pentachlorophenol was done by adding the filter immediately to the bubbler upon completion of collection. The only exception to this was for the collection efficiency experiment.

Analysis

The details of the equipment and instruments used for the analysis and general approach used are described in Attachment C.

Table S297-1

Data Sheet: Pentachlorophenol

Potential Losses Due to Volatilization During Sampling

	µg	Liters		mg/cu m
No room air sampled	242	188.3		1.285
	218	188.0		1.160
	227	188.1		1.207
			mean	1.217
			std dev	0.0631
			CV	0.0519
180 ℓ of room air sampled	170	189.0		0.899
	168	189.8		0.885
	180	188.7		0.954
			mean	0.913
			std dev	0.0365
			CV	0.0400

A description of the procedure for analysis, the preparation of analytical samples for the determination of recovery and the preparation of calibration standards are given in NIOSH Method No. S297 (Reference 4).

The reliability of the analytical method was tested based on the analysis of 18 samples. The analytical samples were prepared by spiking 37-mm Type AA Millipore filters with known aliquots of pentachlorophenol in isopropanol. The aliquots added contained respectively 45, 90 and 180 micrograms of pentachlorophenol representing the equivalent of a 180-liter air sample at 0.5, 1 and 2X the OSHA standard.

After drying, each filter was placed in a 2-ounce ointment jar, 15 ml ethylene glycol was added, the jar sealed with a screw cap equipped with a Teflon film gasket and stored overnight. The following day, prior to analysis by HPLC, 10 ml of methanol was added and the solutions mixed. The data for the analysis of the full set of 18 samples is given in Table S297-2.

Sampling and Analysis

Pentachlorophenol was generated using the Aerosol Generation/Dilution/Sampling System described in Attachments A and B. The Environmental Research Corporation Fluid Atomization Aerosol Generator was used for these studies.

Test atmospheres at a concentration 2X the OSHA standard level were generated by atomization of an isopropanol solution of pentachlorophenol containing 1.5 grams per liter of pentachlorophenol into a dry solvent-free airstream flow. The atomizer air flow was 9 liters per minute; aerosol from the Collison type atomizer was diluted with 108 liters per minute of dry, solvent-free air. The generation/dilution system was operated so that a concentration 2X the OSHA standard level was produced in the main line, then twofold and fourfold dilutions made to obtain concentrations at 1 and 0.5X the OSHA standard levels. All six samples at each of the three test levels were collected simultaneously at 1.5 liters per minute for 120 minutes (180 liters). The 18 samples were analyzed as described in NIOSH Method No. S297 and the data are summarized in Table S297-3.

Particle Size Distribution

Studies were conducted to determine the particle size distribution of the pentachlorophenol aerosol produced in the test chamber. The method used was sampling with an Andersen Cascade Impactor (Particle Fractionation Personnel Sampler) and determination of the amount of pentachlorophenol deposited at each stage by extraction with ethylene glycol and methanol in the usual 3:2 ratio. Analysis was by HPLC.

The data obtained are tabulated below. The effective cutoff aerodynamic diameter in micrometers for each stage are based on manufacturers' quotations which has been determined at a flow rate of 1.4 liters per minute.

Table S297-2

Data Sheet: Pentachlorophenol

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
45.0	45.0	1.000	90.0	92.5	1.028	180.0	189.2	1.051
45.0	43.8	0.973	90.0	88.8	0.987	180.0	187.5	1.042
45.0	45.5	1.011	90.0	86.3	0.959	180.0	190.0	1.056
45.0	42.5	0.944	90.0	80.0	0.889	180.0	184.2	1.023
45.0	45.5	1.011	90.0	91.3	1.014	180.0	183.8	1.021
45.0	42.5	0.944	90.0	100.6	1.118	180.0	198.1	1.101
n =		6			6			6
mean		0.981			0.999			1.049
std dev		0.0315			0.0763			0.02921
CV_1		0.0321			0.0764			0.02785

$\overline{CV_1}$ 0.0505

$\overline{CV_{A+\overline{AMR}}}$ 0.0547

Table S297-3

Data Sheet: Pentachlorophenol

Sampling and Analysis

Test Level	Found			Taken	
	µg	Liters	mg/cu m	mg/cu m*	Recovery
0.5S	46.7	183.8	0.2541	0.257	
	44.3	179.1	0.2473	0.257	
	46.7	179.9	0.2596	0.257	
	49.2	181.6	0.2709	0.257	
	50.4	181.2	0.2781	0.257	
	50.4	178.7	0.2820	0.257	
		n = 6			
		mean	0.2653		1.032
		std dev	0.1383		
		CV_2	0.0521		
1S	125.5	181.5	0.691	0.617	
	119.6	180.9	0.661	0.617	
	111.9	179.7	0.623	0.617	
	107.5	181.5	0.592	0.617	
	111.4	181.5	0.614	0.617	
	113.6	180.5	0.629	0.617	
		n = 6			
		mean	0.635		1.029
		std dev	0.0354		
		CV_2	0.0557		
2S	202.5	183.7	1.102	1.028	
	202.5	183.8	1.102	1.028	
	214.0	184.0	1.163	1.028	
	201.7	184.0	1.096	1.028	
	214.0	183.8	1.164	1.028	
	211.6	182.7	1.158	1.028	
		n = 6			
		mean	1.131		1.100
		std dev	0.0339		
		CV_2	0.0300		
		$\overline{CV_2}$	0.0473		

*Based on the UV analysis of six samples at the OSHA standard. See Table S297-6 for detailed information.

Under the experimental conditions of this test, the flow rate through the impactor was 1.53 liters per minute. The cumulative percent is based on cumulating from the last stage of the impactor.

Stage	Particle Size Range Cut-off Diameter (μm)	μg Pentachlorophenol Found	% Total Particulate	Cumulative %
1	4.7 and up	4.2	5.5	100.0
2	<4.7 - 3.3	5.2	6.8	94.5
3	<3.3 - 2.1	3.6	4.7	87.7
4	<2.1 - 0.65	8.5	11.1	83.0
Backup Filter	0.65	55.0	71.9	71.9
	TOTAL	76.5		

Storage Stability

A storage stability test was conducted to assess whether pentachlorophenol could be successfully stored in an ethylene glycol solution for one week after collection. Twelve samples were collected at a concentration of 0.548 mg/cu m (as determined by analysis of the collected samples). The samples were collected for 120 minutes at an average flow rate of approximately 1.5 liters per minute. Six samples were analyzed immediately and the remainder were stored for one week at ambient conditions. After one week the samples were analyzed as described in Method No. S297. The results of the storage stability test are presented in Table S297-4. The data indicate that pentachlorophenol is stable after 8 days' storage and showed a recovery of 95.3% compared to the one-day-old samples.

Collection Efficiency

Collection efficiency tests were conducted at 1.1 mg/cu m (as determined by analysis of the collected samples). The samples were collected using a filter connected in series to two backup midget bubblers. Each bubbler contained 15 ml of ethylene glycol. The generation conditions used were the same as described under the Sampling and Analysis Section. Samples were collected for 120 minutes at a flow rate of approximately 1.5 liters per minute. The results of the collection efficiency tests are presented in Table S297-5.

Independent Method for Verifying Generator Concentration

An independent method of measuring the concentration of pentachlorophenol was conducted for verification of the results obtained from the validated method. For the independent method samples were collected on 37-mm diameter, 1.0 micrometer polytetrafluoroethylene membrane filters

Table S297-4

Data Sheet: Pentachlorophenol

Storage Stability of Collected Samples

Experiment A: Samples Stored 1 Day

Test Level	Found		
	µg	Liters	mg/cu m
1S	108.2	193.8	0.558
	108.2	189.3	0.572
	105.2	192.0	0.548
	103.8	193.8	0.536
	109.2	193.8	0.563
	98.8	192.7	0.513
		mean	0.548
		std dev	0.0213
		CV_2	0.0389

Experiment B: Samples Stored 8 Days

1S	98.8	193.2	0.511
	94.5	182.2	0.519
	103.8	190.2	0.546
	95.5	186.5	0.512
	96.2	192.0	0.501
	105.0	193.5	0.543
		mean	0.522
		std dev	0.0184
		CV_2	0.0352

Table S297-5

Data Sheet: Pentachlorophenol

Collection Efficiency Tests

µg Found			
Filter and First Bubbler	Second Bubbler	Total	Collection Efficiency
196.8	BDL*	196.8	1.000
195.0	1.5	196.5	0.992
207.4	BDL*	207.4	1.000
191.3	BDL*	191.3	1.000
191.3	BDL*	191.3	1.000
204.2	BDL*	204.2	1.000

Average Collection Efficiency ... 0.999

*BDL = Below detection level of 1.5 µg/25 ml which corresponds to a minimum collection efficiency of 0.992 for a 180-liter collection at 2X the OSHA standard.

Table S297-6

Data Sheet: Pentachlorophenol

Comparison of Validated Method and Independent Method for One-Day-Old Samples

Found by HPLC	-----Found by UV Spectrophotometry-----		
mg/cu m[1]	µg	Liters	mg/cu m
0.691	108.2	180.9	0.598
0.661	105.1	170.6	0.616
0.623	105.8	170.1	0.622
0.592	111.0	174.6	0.636
0.614	109.7	179.7	0.610
0.629	112.0	180.6	0.620
n = 6			n = 6
mean 0.635			mean 0.617
std dev 0.0354			std dev 0.0127
CV_2 0.0557			CV_2 0.0206

[1] Refer to Table S297-3 for detailed information.

connected in series to midget bubblers containing 15 ml of ethylene glycol. After collection, the filters were placed in the bubblers and 10 ml of methanol was added shortly before analysis. An aliquot of the solutions was transferred to 1 cm cuvettes, a drop of concentrated NH_4OH added and the absorbance at 322 nm read on a Beckman DK-1 scanning spectrophotometer. The test atmosphere was generated from a 1.5 g/l solution of pentachlorophenol in isopropanol and samples were collected for 120 minutes at an average flow of 1.5 liters per minute at the OSHA standard level. These samples were collected simultaneously with the 18 samples listed in Table S297-3 and are presented in Table S297-6, together with the OSHA standard level data from the validated method. The mean value for the collected samples analyzed by UV spectrophotometry is used as the "taken" concentration at the OSHA standard level. The "taken" values at the remaining levels were calculated based on measured dilution ratios of 0.25, 0.60 and 1.00 for generation levels of 0.5, 1, and 2X the OSHA standard.

It is to be noted that Millipore type AA filters could not be used for the independent method because of interfering materials extracted from them by the mixed solvent. Furthermore, when Fluoropore filters were added to the mixed solvent, a shift of absorbance peak at 303 mμ to 322 mμ was observed. A drop of concentrated NH_4OH added to standard solution produced the same shift. Adding more NH_4OH to the standards or to the Fluoropore filter containing samples produced no further shift. Therefore one drop of NH_4OH was routinely added to standards and filters containing samples and solution blanks. The shift is believed due to the formation of phenolate ion but no work was done to determine the active ingredient of the Fluoropore filters.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and in the data in Tables S297-2 and S297-3.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation of 0.5, 1 and 2X the OSHA standard for generated samples. The data (Table S297-3) gave a chi squared value of 1.88. Thus Bartlett's test is passed and it is feasible to pool the coefficients of variation and calculate $\overline{CV}_T$.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$$\overline{CV}_1 = 0.0505 \qquad \overline{CV}_2 = 0.0473 \qquad \overline{CV}_T = 0.0717$$

The accuracy of the method was determined by comparison of the average value found by analysis of each set of six samples at each of the three test levels with the taken generator concentration determined as

discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 1.054.

Test Level	mg/cu m Taken	mg/cu m Found	Agreement (Found ÷ Taken)
0.5S	0.257	0.265	1.032
1S	0.617	0.635	1.029
2S	1.028	1.131	1.100
		Average =	1.054

The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, U.S. Government.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

3. W.B. Deichmann, and M.L. Keplinger, "Industrial Hygiene and Toxicology", Vol. II, 2nd ed., John Wiley and Sons, Inc., New York, 1963, p. 1396-1402.

4. Pentachlorophenol, NIOSH Method No. S297, prepared under NIOSH Contract 210-76-0123.

ATTACHMENT A

DILUTION AND SAMPLING SYSTEM FOR
AEROSOL TEST ATMOSPHERES

The dilution and sampling system used to produce the appropriate aerosol test atmospheres is shown schematically in Figure S297-A-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. These branches are designated as A, B, and C in Figure S297-A-1. The dilution and sampling branches A and C are identical and each is equipped with a sampling manifold with six sample ports. The dilution and sampling branch B, on the other hand, is equipped with a sampling manifold with 14 sample ports. Figures S297-A-2 and S297-A-3 show these dilution and sampling branches 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 main line, 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.

Aerosol dilution occurs in the Teflon venturi-shaped inserts shown in Figures S297-A-2 and S297-A-3. Dilution air is injected radially into the venturi throat. The quality of dilution air introduced is fixed by a critical orifice which is connected to one of the constant pressure air manifolds as described in the section on air supply below.

Isokinetic sampling probes, six for branches A and C, and 14 for branch B, are located approximately thirty centimeters downstream of each diluter. The probes convey aerosol to sample collectors (filter cassettes and bubblers) mounted radially around the outside of the sampling section. There is a luer fitting on each sample port to mate with the filter cassette. Sample flow rate 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 S297-A-1).

As is indicated in Figure S297-A-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. For the dilution/sampling branches A and C, there are seven outwardly flowing streams in each branch--one stream is that which flows through the orifice mentioned above (flow rate Q_T) and the other six are the sample streams (total flow rate Q_S). For the dilution/sampling branch B, the flowing streams consist of one which flows through a critical orifice downstream from the sample probes (flow rate Q_T) and fourteen from the sample streams (total flow rate Q_S). There are two inflowing streams--the dilution air stream (flow rate Q_D) and the aerosol stream entering from the main line (flow rate Q_A). The dilution ratio, R, in

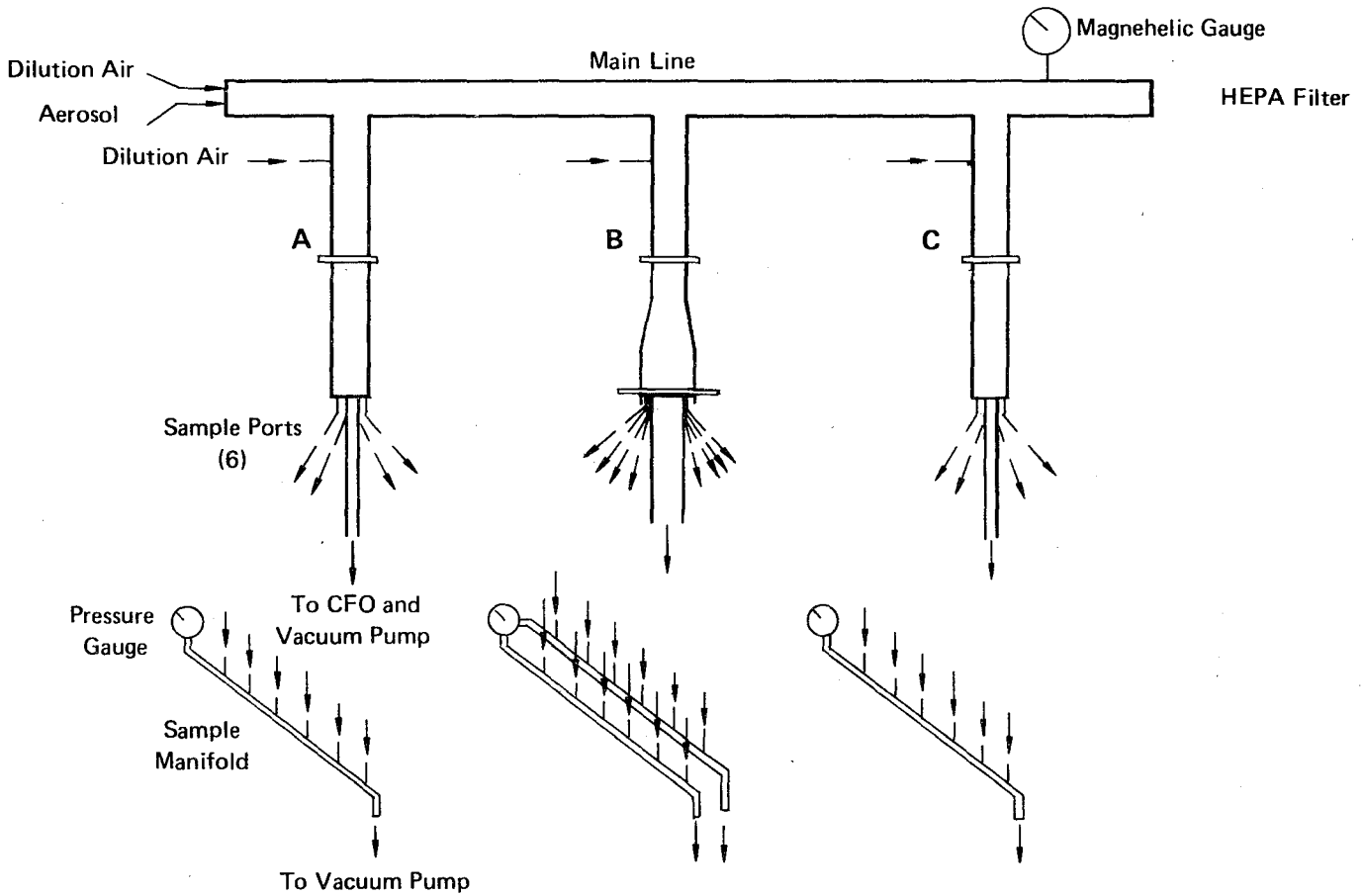


Figure S297-A-1. **AEROSOL DILUTION AND SAMPLING SYSTEM**

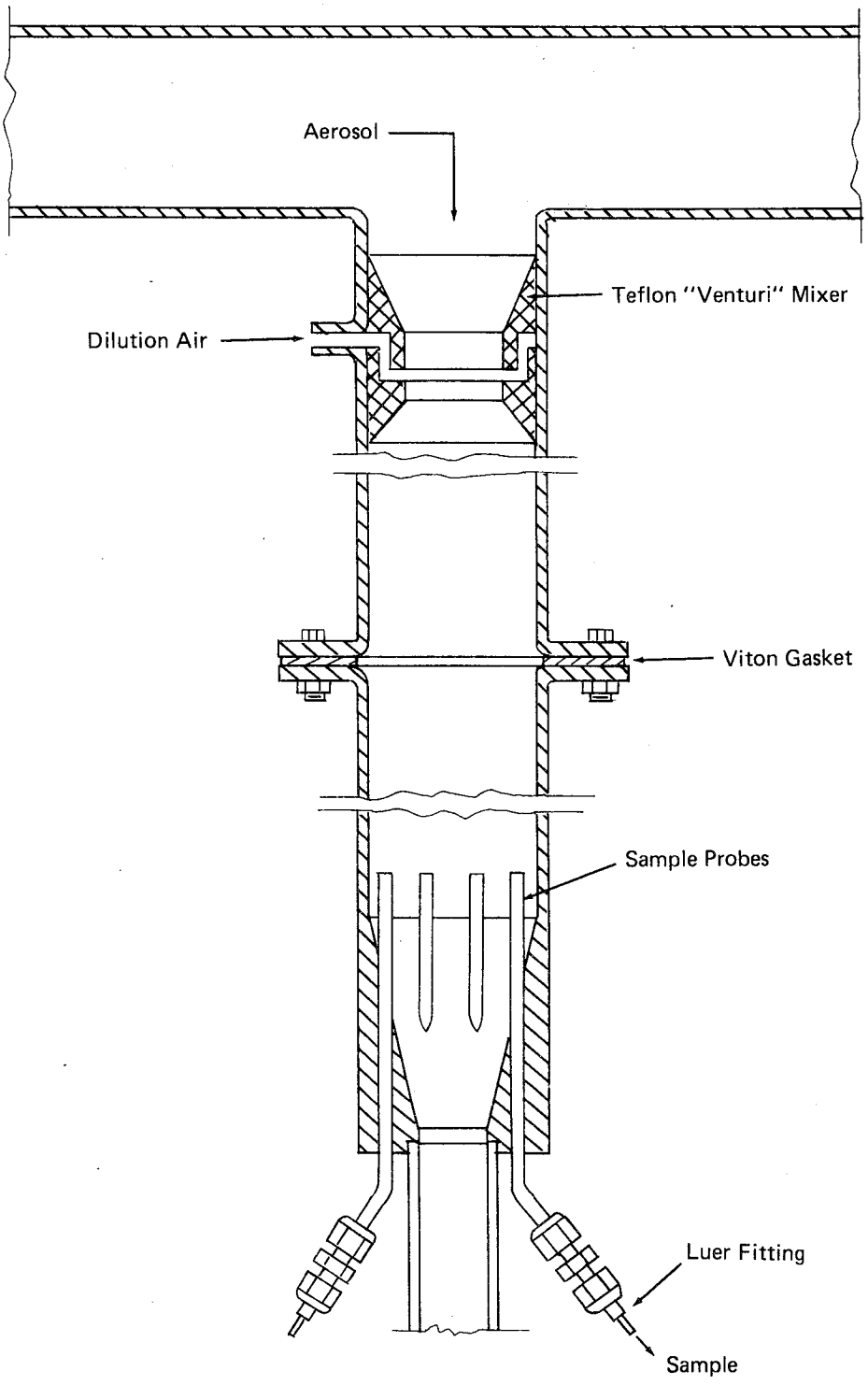


Figure S297-A-2

CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION (BRANCHES A AND C)

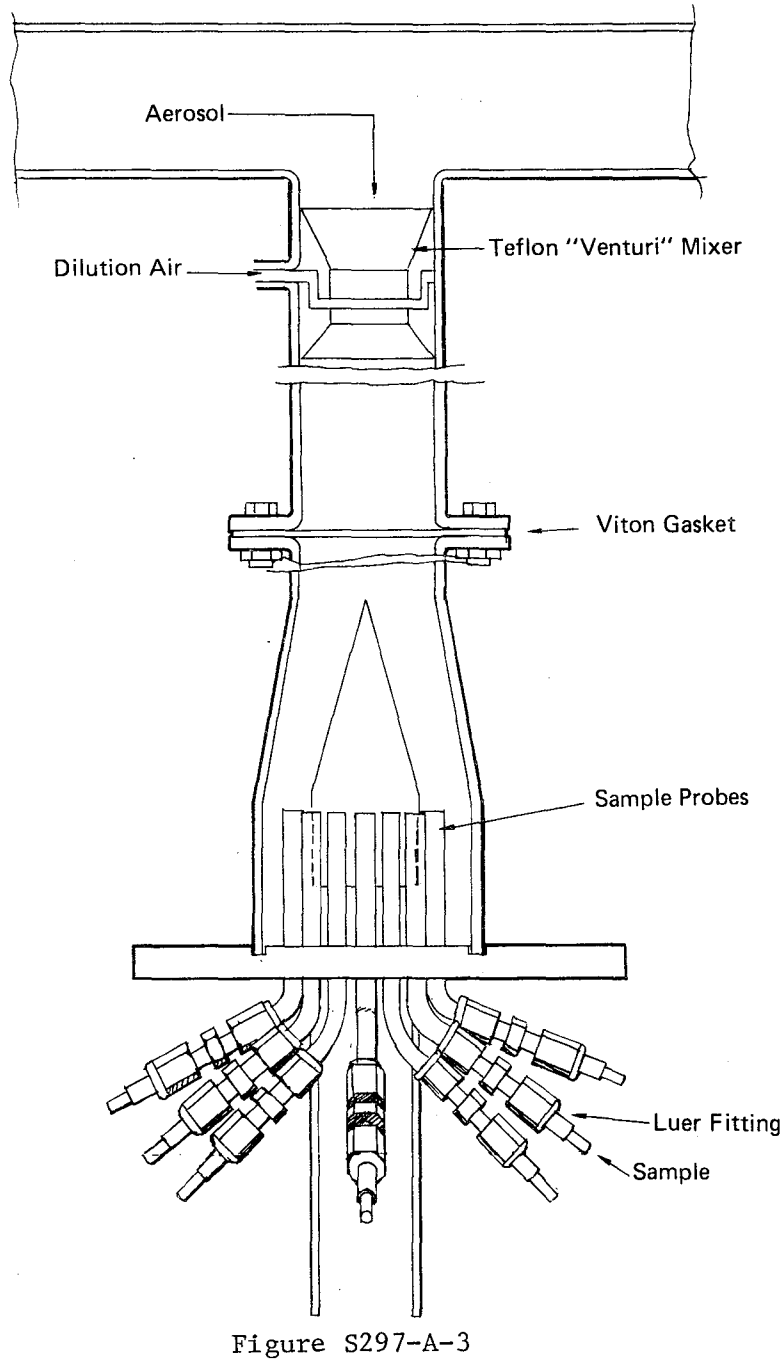


Figure S297-A-3

CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION (BRANCH B)

each branch is given by the correlation:

$$R = \frac{Q_A}{Q_A + Q_D}$$

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 flow rates, 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. No measurable differences (within 1%) in the hydrocarbon concentration were found among the six or fourteen sample ports at any of the three sampling branches. The dilution ratios are rechecked periodically and the typical values are shown in the following section.

The main line flow rate is about 130 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.

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 collections 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).

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 carried out in the trial runs.

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 twenty-four 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 flow rate:	130 liters per minute
Sampling rate:	1.5 liters per minute
Flow rate through dilution/ sampling branch (approximate):	70 liters per minute

Dilution air flow rate (approximate):

2X OSHA standard, Branch C	0
1X OSHA standard, Branch B	36
0.5X OSHA standard, Branch A	53

Dilution ratios measured with hydrocarbon analyzer (Branch C: Branch B: Branch A)	1.00: 0.60: 0.25*

* The dilution ratio is influenced by system pressure and is experimentally determined periodically.

ATTACHMENT B

APPARATUS FOR THE GENERATION OF AEROSOLS

A number of different aerosol generators are available for the production of aerosols. Each of the following generators can readily be used in conjunction with the dilution and sampling system to produce the appropriate aerosol test atmosphere:

- Environmental Research Corporation Fluid Atomization Aerosol Generator Model 7330
- DeVilbiss Model 35A Ultrasonic Nebulizer
- Royco Model WA Aerosol Generator

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.

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.

Ethyl chloride

Analyte:	Ethyl chloride	Method No.:	S105
Matrix:	Air	Range:	1590-6500 mg/cu m
OSHA Standard:	1000 ppm (2600 mg/cu m)	Precision ($\overline{CV}_T$):	0.096
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC/FID	Validation Date:	1/20/78

1. Principle of the Method

1.1 A known volume of air is drawn through a large charcoal tube to trap the ethyl chloride gas present. The sampling train consists of two separate tubes--a front adsorbing tube and a backup tube; this sampling arrangement is necessary to prevent sample migration during storage.

1.2 The charcoal in each tube is transferred to a serum vial and sealed with a septum and a laquered aluminum seal. The ethyl chloride is desorbed with carbon disulfide and analyzed by gas chromatography.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1586-6500 mg/cu m at an atmospheric temperature of 24.5°C and atmospheric pressure of 770.8 mm Hg using a 3-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity at the 2S test level determined at 90% relative humidity. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of ethyl chloride and other substances in the air (see Section 5.2).

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 1586-6500 mg/cu m was 0.0955. This value corresponds to a 248.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.4% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

4.3 The data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. The sample capacity of the charcoal tube is dependent on humidity. When an atmosphere at 90% relative humidity containing 5560 mg/cu m of ethyl chloride was sampled at a flow rate of 0.0576 liter per minute, 5% breakthrough was observed after 74 minutes (capacity = 4.26 liters or 23.69 mg).

To minimize the probability of overloading the sampling tube, the sample size recommended is less than 2/3 the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard level.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This pressure drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment

6.1.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate (Reference 11.3).

6.1.2 Sampling Tubes. The sampling train consists of two separate charcoal tubes connected in series. The tubes are glass tubes with both ends flame-sealed, 10-cm long with an 8-mm O.D. and a 6-mm I.D. The front tube contains 400 mg of 20/40 mesh activated coconut charcoal; the backup tube, 200 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the two tubes in series must be less than one inch of mercury at a flow rate of 1 liter per minute.

This sampling train can be prepared by modifying commercially available charcoal tubes as follows. For the front tube--break off exit end of a large tube and using pointed tweezers remove the urethane foam plug and the backup charcoal section; push in snugly remaining plug and charcoal to minimize channeling. For the backup tube--similarly break off inlet end of a second large tube and remove retaining plug and the front charcoal section; again push together remaining plug and charcoal. The front tube is connected to the backup tube with a minimal piece of plastic or rubber tubing.

Note that this sampling tube scheme is necessary to minimize probable sample migration effects upon storage.

6.1.3 Thermometer.

6.1.4 Barometer.

6.1.5 Stopwatch.

6.2 Gas chromatograph equipped with a flame ionization detector.

6.3 Column, 20-ft x 1/8-in stainless steel packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Glass serum vials for desorption, 3-ml, molded to take 13-mm rubber septa and 13-mm aluminum seals.

6.5.1 Rubber septa, 13-mm.

6.5.2 Lacquered aluminum seals or caps, 13-mm.

6.5.3 Hand crimper, 13-mm, or equivalent for properly sealing the vial assembly.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

6.6 Microliter syringes, 500-microliter and other convenient sizes for making internal standard stock solution.

6.7 Gas-tight syringes, 10-ml and other convenient sizes for making standards.

6.8 Syringe, 5.0-ml capacity for adding the carbon disulfide used for desorption.

6.9 Syringe needle, 1.5-inch, 22-gauge or other convenient size.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Carbon disulfide, chromatographic quality.

7.2 Ethyl chloride, 99.7%.

7.3 Nonane or other suitable internal standard. The appropriate solution of the internal standard is prepared in carbon disulfide.

7.4 Nitrogen, purified.

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling train in the line assembled as noted in Section 6.1.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube (3-mm). Prepare and assemble as described in Section 6.1.2. Connect the front 400-mg tube to the 200-mg backup tube with a short piece of tubing.

8.3.2 The tube containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal sampling train should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the front charcoal tube.

8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate of 0.05 liter per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The front charcoal tube should be separated from the backup tube immediately after sampling. Both tubes must be labeled appropriately and capped with the supplied plastic caps.

8.3.8 One set of charcoal tubes (a 400-mg tube and a 200-mg backup tube) should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This set of tubes should be labeled as a blank. Submit one blank for every batch of 10 samples.

8.3.9 Unused, capped charcoal tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency varies from one batch of charcoal to another. Record the batch number of the charcoal used.

8.3.10 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file and broken open. The glass wool is removed and discarded. The charcoal in the front tube is transferred to a 3-ml serum vial and the vial is sealed with the rubber septum and the aluminum cap with the aid of the crimper. The charcoal in the backup tube is transferred to another serum vial and handled in a similar manner.

8.4.2 Desorption of Sample. Immediately before desorption, lift up or remove the removable portion of the aluminum cap to expose a portion of the septum without destroying the seal. Insert a syringe needle through the septum keeping the tip of the needle just below the surface of the septum in the vial. (This needle serves as a vent to prevent pressure buildup in the vial when carbon disulfide is added.) Add 2.0 ml of carbon disulfide or 2.0 ml of internal standard stock solution into the sample-containing vial with the aid of a syringe. After the carbon disulfide addition, remove the needle being used as a vent. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

If an automatic sample injector is used, transfer the sample solution from the desorption vial to the automatic sample injector vial with the aid of a syringe. Seal the sample injector vial with the Teflon-lined septum and screw cap.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 160°C injector temperature
5. 190°C manifold temperature (detector)
6. 110°C column temperature

A retention time of approximately 3.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6. The retention time for the internal standard, nonane, is approximately 4.5 minutes.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The

solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of charcoal used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of ethyl chloride found in the samples. The desorption efficiency must be determined for each concentration level of ethyl chloride found in the samples analyzed.

The analytical samples are prepared as follows: Activated charcoal (400 mg), from the same lot used in collecting samples, is packed into glass tubes (10 cm x 8 mm O.D. x 6 mm I.D.). If the commercially available charcoal tubes are used, break off both ends and remove the backup sections. These tubes are labeled and weighed. The appropriate volume of ethyl chloride is slowly injected directly onto the charcoal with a gas-tight syringe. These tubes are weighed again, capped immediately, and stored. The weight (mg) of ethyl chloride added is calculated by taking the difference between the two weights.

For the validation studies conducted to determine the precision and accuracy of this method, six tubes at each of three concentration levels (0.5, 1, and 2X the OSHA standard) were prepared by adding an amount of ethyl chloride equivalent to that present in a 3-liter sample at the selected level. This required the addition of 1.5, 3, and 6 ml of ethyl chloride gas into charcoal tubes. The tubes were allowed to stand at least over-

night to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the analytical samples. A parallel blank tube was treated in the same manner except that no sample was added to it. Desorption and analysis experiments were performed on the analytical samples as described in Sections 8.4.2 to 8.4.5.

The desorption efficiency (D.E.) equals the average in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is expected to be dependent on the amount of ethyl chloride collected on the charcoal. Plot the desorption efficiency versus weight of ethyl chloride found. This curve is used in Section 10.4 to correct for adsorption losses. If the desorption efficiency is greater than 95% no correction should be applied.

9. Calibration and Standards

9.1 Seal a 3-ml serum vial, using a rubber septum and aluminum cap with the aid of a crimper.

9.2 Insert a syringe needle through the septum keeping the tip just below the surface of the septum, in order to provide a vent. With the aid of a syringe, inject 2.0 ml of carbon disulfide (or 2.0 ml of internal standard solution) into the vial. Remove the needle used as a vent.

9.3 Immediately before adding the ethyl chloride gas, withdraw an amount of air from the sealed vial equal to the volume of the gas to be added. Label and weigh the vial and record the weight. An appropriate amount of ethyl chloride is bubbled slowly into the carbon disulfide using a gas-tight syringe. The syringe needle should be immersed in the carbon disulfide during discharge of the ethyl chloride from the syringe.

9.4 The vial is weighed again and the weight (mg) of the ethyl chloride is calculated by taking the difference between the weight before and after the addition of ethyl chloride gas.

9.5 The concentration of standards can be expressed in terms of mg ethyl chloride per 2 ml of carbon disulfide. This unit is convenient because samples are desorbed in 2 ml of carbon disulfide.

9.6 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/2 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 40% of the concentration at the OSHA standard. The analyte concentration in mg per 2.0 ml is plotted versus the area ratio of the analyte to that of the internal standard.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front (400-mg) sample tube
mg blank = mg found in front (400-mg) blank tube

A similar procedure is followed for the backup tube.

10.3 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (See Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{64.52} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

p = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
64.52 = molecular weight of ethyl chloride
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-0231-2.

11.2 Backup Data Report for Ethyl chloride, prepared under NIOSH Contract No. 210-76-0123.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Sampling Data Sheet No. S105
January 20, 1978

Substance

Ethyl chloride

Standard

8-hour time-weighted average: 1000 ppm (2600 mg/cu m)

Analytical Method

A known volume of air is drawn through two charcoal tubes connected in series to trap the ethyl chloride gas present. The ethyl chloride is desorbed from the charcoal with carbon disulfide, and the sample is analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 1586-6500 mg/cu m for a 3-liter sample at 24.5°C and 770.8 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The equipment needed for sampling ethyl chloride includes a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%, at a flow rate of 0.05 liter per minute and a charcoal sampling tube series. The pump is calibrated with a representative sampling tube series in line.

The sampling train consists of two separate charcoal tubes connected in series. The tubes are glass tubes with both ends flame-sealed, 10-cm long with an 8-mm O.D. and a 6-mm I.D. The front tube contains 400 mg of 20/40 mesh activated coconut charcoal; the backup tube, 200 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the two tubes in series must be less than one inch of mercury at a flow rate of 1 liter per minute.

This sampling train can be prepared by modifying commercially available large charcoal tubes as follows: for the front tube--break off exit end of a large tube and using pointed tweezers remove urethane foam plug and the backup charcoal section; push in snugly remaining plug and charcoal to minimize channeling. For the backup tube--similarly break off inlet end of a second large tube and remove retaining plug and the front charcoal section; again push together remaining plug and charcoal. The front tube is connected to the backup tube with a minimal piece of plastic or rubber tubing.

Note: This sampling tube scheme is necessary to minimize probable sample migration during storage.

Sample Size

A sample size of 3 liters is recommended. Sample at a flow rate of 0.02-0.05 liter per minute.

Sampling Procedure

1. Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes (3-mm). Prepare and assemble tubes as described in sampling equipment section. Connect the front 400-mg tube to the 200-mg backup tube with a short piece of tubing.

2. The tube containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump. The charcoal tube series should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the front charcoal tube.

4. A low flow rate pump is used. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. The two tubes must be separated and each tube recapped tightly. The tubes should be identified accordingly to distinguish the corresponding pair of front and backup sampling tubes.

6. One set of charcoal tubes (a 400-mg tube and a 200-mg backup tube) should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This set of tubes should be labeled as a blank. Submit one blank for every batch of 10 samples.

7. Unused, capped charcoal tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency varies from one batch of charcoal to another. Record the batch number of the charcoal used.

Special Considerations

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Due to the high resistance of the charcoal tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than 8 hours of sampling should be done without first fully recharging the battery.

Shipping Instructions

Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

Reference

Ethyl chloride, NIOSH Method No. S105.

Backup Data Report, No. S105
January 20, 1978

Substance:	Ethyl chloride
OSHA Standard:	1000 ppm (2600 mg/cu m)
Chemical Used for Validation	Ethyl chloride, 99.7%, Matheson Gas Company

General Considerations

The method for ethyl chloride has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 $\pm$ 10% and the $\overline{CV}_T$ of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for the validation of a method for ethyl chloride included the following experimental studies:

- Analysis of a total of 18 analytical samples (6 samples at each of the three test levels--0.5, 1, and 2X the OSHA standard) spiked with the appropriate amount of ethyl chloride to represent a sample volume equal to 3 liters,
- Analysis of a total of 18 samples collected from dynamically generated test atmospheres (6 samples at each of the three test levels--0.5, 1, and 2X the OSHA standard) for the same sample volume as above,
- Determination of the breakthrough capacity of activated coconut charcoal at high relative humidity,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following appropriate sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Principle of Method

The procedure for collection and analysis of air samples of ethyl chloride is described in NIOSH Method No. S105. This method consists of collection of ethyl chloride on activated coconut charcoal, desorption with carbon disulfide, and analysis of the resulting solution by gas chromatography with a flame ionization detector. A sample size of 3 liters is recommended.

Analysis

The details of the equipment and instruments used for the analysis and the general approach used are described in Attachment A.

A detailed description of the procedure for analysis, the preparation of the analytical samples for the determination of desorption efficiency, and the preparation of calibration standards are given in NIOSH Method No. S105.

It should be noted that the desorption procedure described should be followed carefully in order to minimize sample losses. The vial containing the chemical sample must be sealed before adding the carbon disulfide to prevent losses due to evaporation of ethyl chloride caused by the heat of desorption.

The reliability of the analytical method tested was based on the analysis of 18 analytical samples. These samples were prepared by spiking 400 mg of activated coconut charcoal with 1.5, 3.0, and 6.0 ml of ethyl chloride gas, representing the equivalent of a 3-liter air sample at 0.5, 1, and 2X the OSHA standard.

The data for the full set of analytical samples are shown in Table S105-1.

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachments B and C. A steady stream of ethyl chloride was delivered from a gas cylinder via a rotameter at a flow rate of 263.3 ml/min or 706 mg/min to a dry air stream flowing at a rate of 0.1086 cu m/min.

The three sample lines were maintained at measured dilution ratios of 0.244, 0.520 and 1.000 to produce the 0.5, 1, and 2X OSHA standard test levels. The delivery rate of the ethyl chloride was determined by calibrating the rotameter using a dry gas test meter; a soap-bubble flow meter could not be used because ethyl chloride does not support formation of a bubble. The data are shown in the section on Independent Method of Verifying Generator Concentration.

The samples were collected on charcoal tubes with 400 mg in the front section and 200 mg in the backup section. The backup sections were removed immediately after collection to prevent any migration of the

Table S105-1

Data Sheet: Ethyl Chloride

Analysis

Level	0.5S			1S			2S	
mg added	mg found	Recovery	mg added	mg found	Recovery	mg added	mg found	Recovery
3.46	3.67	1.061	7.29	7.42	1.018	15.37	14.90	0.969
3.56	3.47	0.975	7.43	7.53	1.013	14.94	14.89	0.997
3.46	3.62	1.046	7.09	7.43	1.048	15.20	14.59	0.960
3.70	3.71	1.003	7.34	7.57	1.031	15.37	14.86	0.967
3.51	3.60	1.026	7.13	7.35	1.031	15.32	14.64	0.956
3.41	3.66	1.073	7.15	7.39	1.034	15.35	14.79	0.964
n =		6			6			6
mean		1.031			1.029			0.969
std dev		0.0370			0.01242			0.01458
CV_1		0.0359			0.01207			0.01505

$\overline{CV}_1$ 0.02353

$\overline{CV}_{A+\overline{DE}}$ 0.02541

ethyl chloride. Twenty-four samples were collected simultaneously at 0.05 liter per minute for 60 minutes (3 liters). Eighteen samples, six at each of the three test levels, were analyzed after one day, as described in Section 8.4 of the NIOSH Method No. S105; the backup sections of the samples collected at 2X the OSHA standard level were analyzed similarly. The six remaining samples were stored and analyzed after seven days.

The data obtained for the 18 samples analyzed after one day are shown in Table S105-2. The average recovery was 98.6%. No trace of ethyl chloride was found in the backup sections.

Storage Stability

Studies were done to assess the stability of ethyl chloride samples upon storage for one week at atmospheric conditions. For these studies, six samples collected at the OSHA standard level were stored for seven days and analyzed. These results were compared with the data for the six samples collected simultaneously at the OSHA standard and analyzed after one day. The data for these samples are shown in Table S105-3. The results indicate that the samples are stable over a seven-day period; the average recovery was 97.9% for the one-day-old samples vs. 99.7% for the seven-day-old samples.

Based on information in the Ethyl chloride Failure Report (Reference 4), charcoal tubes connected in series are recommended in order to prevent migration losses.

Breakthrough Tests

Breakthrough tests were done in an atmosphere where the relative humidity was 90%. Breakthrough is defined as the time at which the effluent concentration from the collection tube (containing 400 mg of charcoal) is 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, when the substance of interest in the test atmosphere is at the 2X OSHA standard level.

The procedures for determining breakthrough in high relative humidity atmospheres together with the description of the equipment used are described in the section on Breakthrough Studies in Attachment B.

Breakthrough at 90% relative humidity occurred in 74 minutes when sampling at a flow rate of 0.0576 liter per minute with a main line concentration of 5560 mg/cu m. The capacity of the charcoal was calculated to be 23.69 mg or 4.26 liters.

These tests were conducted at an atmospheric temperature of 21°C and an atmospheric pressure of 770.8 mm Hg. A 3-liter maximum sample size

Table S105-2

Data Sheet: Ethyl chloride
Sampling and Analysis

Test Level	Found			Taken	Recovery
	mg	Liters	mg/cu m	mg/cu m	
0.5S	6.26	3.84	1630	1586	
	5.95	3.86	1541	1586	
	6.47	4.07	1590	1586	
	6.49	4.21	1542	1586	
	6.43	4.22	1524	1586	
	5.89	3.75	1571	1586	
		n = 6			
		mean	1566		0.987
		std dev	39.1		
		CV_2	0.02497		
1S	10.75	2.89	3720	3380	
	10.56	3.87	2729	3380	
	13.65	3.91	3490	3380	
	12.66	3.78	3350	3380	
	12.30	3.81	3230	3380	
	12.77	3.84	3330	3380	
		n = 6			
		mean	3310		0.979
		std dev	331		
		CV_2	0.1000		
2S	22.85	3.75	6090	6500	
	24.84	3.79	6550	6500	
	20.77	3.75	5540	6500	
	25.37	3.90	6510	6500	
	25.94	3.90	6650	6500	
	27.94	3.79	7370	6500	
		n = 6			
		mean	6450		0.992
		std dev	610		
		CV_2	0.0946		
		$\overline{CV_2}$	0.0808		

Table S105-3

Data Sheet: Ethyl chloride

Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found			Taken	Recovery
	mg	Liters	mg/cu m	mg/cu m	
1S	10.75	2.89	3720	3380	
	10.56	3.87	2729	3380	
	13.65	3.91	3490	3380	
	12.66	3.78	3350	3380	
	12.30	3.81	3230	3380	
	12.77	3.84	3330	3380	
		mean	3310		0.979
		CV_2	0.1000		

Expt. B: Samples Stored 7 Days

1S	12.64	3.86	3270	3380	
	12.84	3.89	3300	3380	
	13.66	4.05	3370	3380	
	13.16	3.78	3480	3380	
	13.27	3.88	3420	3380	
	10.28	3.06	3360	3380	
		mean	3370		0.997
		CV_2	0.02281		

is recommended for ethyl chloride. This sample size will yield 15.6 mg of ethyl chloride at 2X the OSHA standard level, 2000 ppm or 5200 mg/cu m at 25°C and 760 mm Hg.

Independent Method of Verifying Generator Concentration

The generator concentration of ethyl chloride was established by experimentally determining the gas delivery rate (in mg/min) into a measured dilution air flow (in cu m/min) and calculating the concentration of the 2S line from these values (in mg/cu m). The concentration of the 0.5S and 1S lines can be calculated by measuring the dilution ratio of the 0.5S and 1S line relative to the 2S (main) line.

The delivery rate of ethyl chloride gas into the generation system was determined by calibrating a rotameter using a Singer Dry Gas meter. The data obtained for the delivery rate in ml/min at 24.5°C and 770.8 mm Hg are shown below:

	247.9
	247.8
	254.0
	275.8
	277.2
	277.3
Average:	263.3 ml/min or 706 mg/min

The corrected main line flow was found to be 0.1086 cu m/min at the respective atmospheric temperature and pressure conditions of 24.5°C and 770.8 mm Hg. In addition, the sample lines were maintained at measured dilution ratios of 0.2440, 0.520, and 1.000 to produce test levels at 0.5, 1, and 2X the OSHA standard.

Based on these data, the "taken" generator concentration at the 0.5, 1, and 2S lines are respectively: 1586, 3380, and 6500 mg/cu m.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S105-1 and S105-2.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1, and 2X the OSHA standard for generated samples. The data (Table S105-2) gave a chi squared value of 7.38, indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$\overline{CV}_1 = 0.02353$ $\overline{CV}_2 = 0.0808$ $\overline{CV}_T = 0.0955$

The accuracy of the method was determined by comparison of the average value found by analysis of six samples at each of the three test levels with the Taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 98.6%.

Test Level	mg/cu m Taken	mg/cu m Found	Agreement Found ÷ Taken
0.5S	1586	1566	98.7
1S	3380	3310	97.9
2S	6500	6450	99.2
		Average:	98.6%

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the desorption efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, U.S. Government.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-0231-2.

3. Ethyl chloride, NIOSH Method No. S105, prepared under NIOSH Contract No. 210-76-0123 with validation date January 20, 1978.

4. Failure Report on Ethyl chloride, No. S105, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

ATTACHMENT A

GAS CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the gas chromatography (GC) methods consists of a Varian 2700 Series Gas Chromatograph, a Varian Model 8000 automatic sample injector and a Spectra Physics System 1 computing integrator.

The Varian 2700 is a dual column unit equipped with a flame ionization detector and a photoionization detector (Hnu Systems, Inc.). The unit can be set for isothermal or for linear temperature program operation, either manually or automatically.

The Model 8000 automatic sample injector is mounted horizontally on the Varian 2700 and can readily be moved to align with either of the two injection ports. 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 dry nitrogen, and a control unit which permits total automation in a closed loop form with a computer. For this program, the syringe injector has been set to deliver 5 microliters of sample solution. The unit has been tested to verify that sample to sample cross-contamination does not occur and that the reproducibility of the sample injection is adequate. Periodic checks have been carried out on six or twelve repetitive injections of a standard solution in carbon disulfide and the observed standard deviation of the integrated peak areas is never greater than 2.5%.

All peak area measurements were done with the System 1 computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System 1 also has the capability to calculate sample concentration directly once the calibration factor has been determined.

Approach

The internal standard method (relative area measurements) has been used for this program not only because of its inherently better reproducibility than the external standard method (absolute area measurements) but also as a safeguard against any problems that could arise during the periods of unattended overnight operation. Such problems include detector response variations and the partial clogging of the sample injector loop which can give rise to variability in sample size injections. These clogging effects are caused by the very fine solid sorbent particles which remain suspended in the solution.

A comparative study of the reproducibility of the absolute area and the relative area measurements was performed using sec-butyl acetate (1.5 mg/ml) and undecane as internal standard. The precision of 12 successive determinations was 1.7% based on absolute areas and 0.4% using relative areas.

The choice of an internal standard has been restricted to those compounds which present minimal adsorption losses on the specific solid sorbent used. Experiments have been run to verify adsorption losses by determining the integrated areas of analyte and internal standard in a calibration solution and comparing these areas with the respective areas obtained when 1.0 ml (or other appropriate volume) aliquots of the same calibration solution are added to the appropriate amounts of solid sorbent. (Use the same weight of solid sorbent as that used for sampling.) The ideal internal standard is one which does not show any significant decrease in area due to the solid sorbent addition; this phenomenon is dependent on the interactive characteristics of the internal standard, the solid sorbent and the desorption solvent.

ATTACHMENT B

VAPOR GENERATION

Controlled Gas Injection

When gaseous substances are to be tested the desired concentration of vapor is generated by a controlled flow injection. When a cylinder of gas is used, the gas is fed into the dilution/sampling system through a calibrated gas rotameter. The delivery rate is calibrated by either a dry gas meter or bubble meter depending on the flow rate used.

Calculation of Main Line Concentration

The calibrated gas delivery rate in ml/min is converted by ideal gas law calculations to units of mg/min. The Main Line concentration is then determined by dividing the delivery rate in mg/min by the Main Line flow rate in cu m/min. This gives the concentration generated in units of mg/cu m.

If a gas mixture is used for generation, the exact content of the cylinder is determined by chemical analysis. A correction factor is then applied to the calibrated delivery rate and the Main Line concentration calculated as above.

ATTACHMENT C

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S105-C-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 sampling devices 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, 0.017 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) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

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

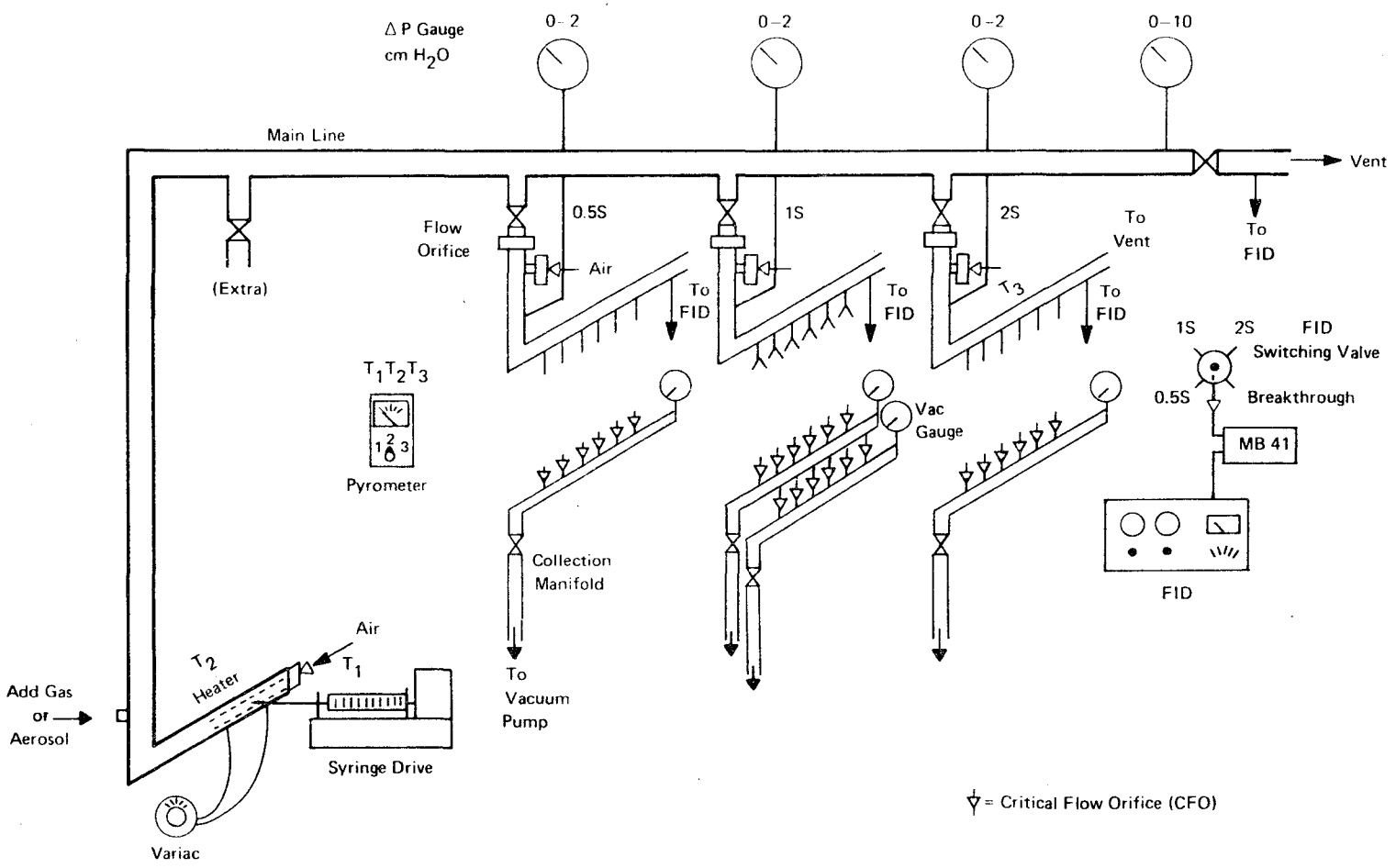


Figure S105-C-1. Vapor Generation/Dilution/Sampling System

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 sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. 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 a 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 (1.5 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

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 0.1086 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.

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	0.499	0.227

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

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 400 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. 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. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) 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.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S105-C-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.

2. Sample delivery rate is determined by appropriate calibration.

3. Sample is fed into Main Line until vapor concentration equilibrium is established.

4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.

5. The four sets of six samples from the three concentration levels are collected simultaneously.

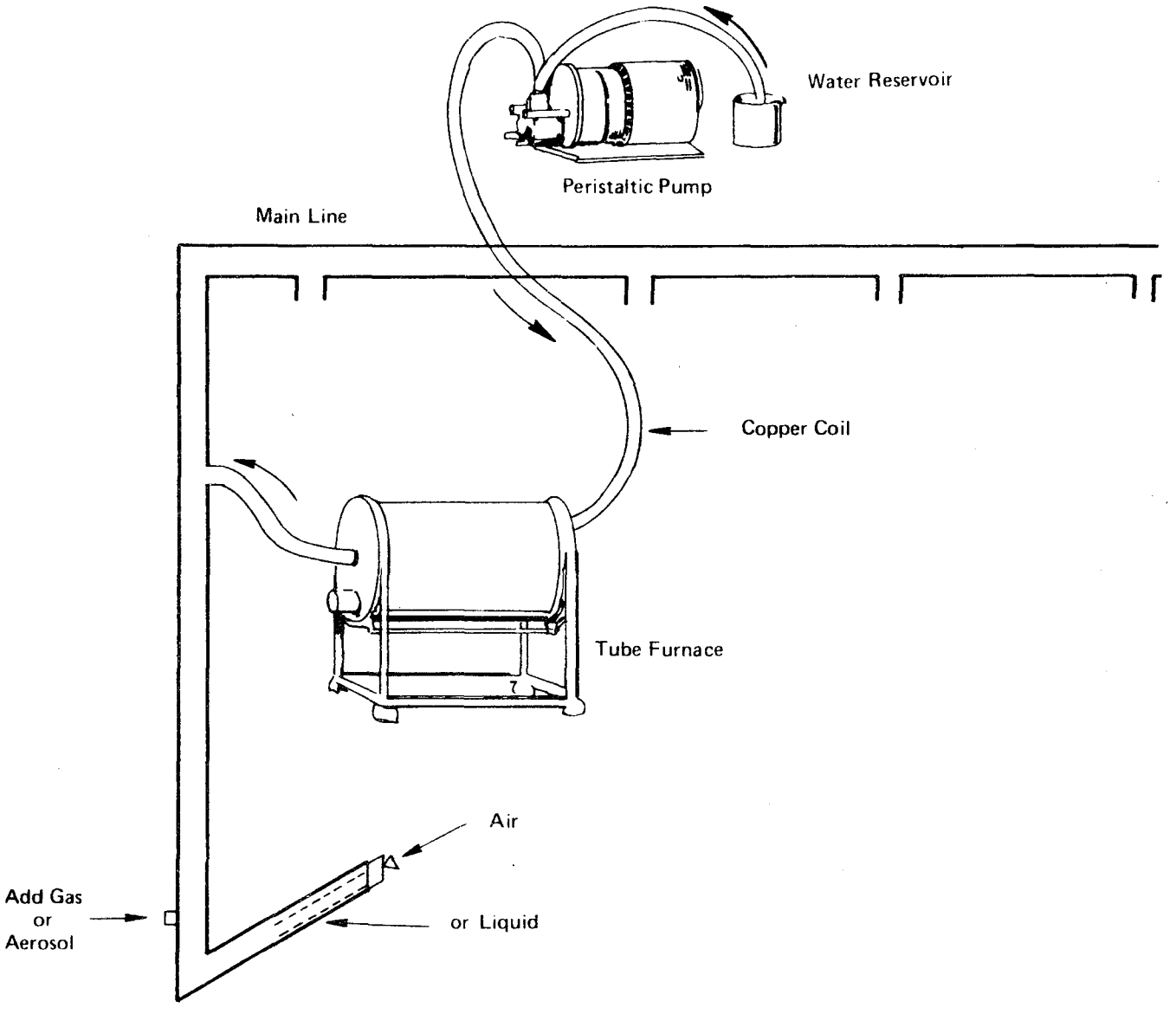


Figure S105-C-2. Generation of High Humidity Atmospheres

Nitroethane

Analyte:	Nitroethane	Method No.:	S219
Matrix:	Air	Range:	147-600 mg/cu m
OSHA Standard:	100 ppm (310 mg/cu m)	Precision ($\overline{CV}_T$):	0.060
Procedure:	Adsorption on XAD-2, desorption with ethyl acetate, GC/FID	Validation Date:	1/20/78

1. Principle of the Method

1.1 A known volume of air is drawn through a series of tubes containing XAD-2 resin to trap the organic vapors present. The sampling train consists of two separate tubes--a front adsorbing tube and a backup tube; this sampling arrangement is necessary to prevent sample migration during storage.

1.2 The XAD-2 in each tube is transferred to respective vials and the nitroethane is desorbed with ethyl acetate. An aliquot of this sample solution is injected into a gas chromatograph equipped with a flame ionization detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 147.4-604 mg/cu m at an atmospheric temperature of 22°C and an atmospheric pressure of 777 mm Hg using a 3-liter sample volume.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the XAD-2 resin. This capacity varies with the concentrations of nitroethane and other substances in the air (see Section 5.2).

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 147.4-604 mg/cu m was 0.0602. This value corresponds to an 18.66 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analytical method was 2.2% lower than the "true" concentration for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When an atmosphere at 90% relative humidity containing 585 mg/cu m of nitroethane was sampled at 0.049 liter per minute, 5% breakthrough was observed after 98 minutes (capacity = 4.8 liters or 2.8 mg). The sample size recommended is two-thirds the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X the OSHA standard to minimize the probability of overloading the sampling tube.

5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling at 0.05 liter per minute for 60 minutes. The pump must be accurate to within $\pm$5% at the recommended flow rate.

6.1.2 Sampling Tubes. The sampling train consists of two separate XAD-2 tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with a 10-mm O.D. and a 8-mm I.D. The XAD-2 used must be prewashed with ethyl acetate and dried. The front tube contains 600 mg XAD-2; the backup tube, 300 mg. A plug of silylated glass wool is placed at each end of the sorbent tubes. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

Note that this sampling tube scheme is necessary to prevent sample migration upon storage.

6.2 Gas chromatograph with a flame ionization detector.

6.3 Column, 20-ft x 1/8-in stainless steel, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Microliter syringes, 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots.

6.6 Pipettes, 2-ml, delivery type.

6.7 Volumetric flasks, 25-ml or other convenient sizes for making standard solutions.

7. Reagents

Wherever possible, reagents used should be ACS reagent grade or better.

7.1 Nitroethane, chromatographic quality.

7.2 Ethyl acetate, reagent grade.

7.3 1-Hexanol, 99% or other suitable internal standard. The appropriate solution of the internal standard is prepared in ethyl acetate.

7.4 Pre-cleaned Resin. XAD-2 resin (20/50 mesh) can be obtained from Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Twenty-four hour extractions are then performed successively with water, methanol, and methylene chloride. Resin has been prepared in this manner using charges of about 700 grams of resin and 1.5 liters of each solvent. The resin is dried in a fluidized bed using nitrogen gas

at room temperature from a liquid nitrogen cylinder. The drying process is terminated when essentially no solvent is detected in the effluent. A final quality control check is performed by desorbing a portion of the resin and analyzing the resulting solution by gas chromatography. Residual solvent should be less than 1000 ppm in concentration. Finally, several washings with ethyl acetate are recommended to reduce possible interferences to a minimum when the sorbent is desorbed with this solvent. This can be done in a beaker of the appropriate volume. The resin is then air-dried.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes (4-mm). Connect the front 600-mg tube to the 300-mg backup tube with a short piece of tubing.

8.3.2 The tube containing 300 mg of XAD-2 is used as a backup and should be positioned nearest the sampling pump. The XAD-2 tube series should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the front XAD-2 tube.

8.3.4 A sample size of 3 liters is recommended. Sample at a known flow rate between 0.03 to 0.05 per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information

to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 Immediately after sampling the two XAD-2 tubes must be separated and each tube capped with the supplied plastic caps. The tubes should be identified to distinguish each corresponding pair of front and backup tubes.

8.3.6 One set of XAD-2 tubes (a 600-mg tube and a 300-mg backup tube) should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This set of tubes should be labeled as a blank. Submit one blank for every ten samples.

8.3.7 Unused XAD-2 tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency may vary from one batch of XAD-2 to another. Record the batch number of the XAD-2 used.

8.3.8 Capped XAD-2 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each tube is scored with a file and broken open. The glass wool is removed and discarded. The XAD-2 in each tube is transferred to a 5-ml screw-cap sample vial. Each tube is analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 ml of ethyl acetate is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 ml of ethyl acetate containing a known amount of internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 160°C injector temperature
5. 200°C manifold temperature (detector)
6. 120°C column temperature

A retention time of approximately nine minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately seventeen minutes.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of XAD-2 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% for a loading equivalent to a collection at the OSHA standard level. If the desorption efficiency is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of nitroethane found in the samples.

The analytical samples are prepared as follows: XAD-2 resin, equivalent to the amount in the front section (600-mg), is measured into a 5-ml screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of nitroethane in ethyl acetate (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µl aliquot is used to prepare the analytical samples.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) were prepared by adding an amount of nitroethane equivalent to a 3-liter sample at the selected level. A stock solution containing 235.1 milligrams of nitroethane per milliliter of ethyl acetate was prepared. Two, four and eight microliter aliquots of the solution were added to the XAD-2 resin vials to produce 0.5, 1, and 2X the OSHA standard level. The analytical samples were allowed to stand overnight to assure complete adsorption of the analyte onto the resin. A parallel blank vial was treated in the same manner except that no sample was added to it.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 ml of ethyl acetate with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of ethyl acetate containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in µg recovered from the vial divided by the weight in µg added to the vial, or

$$\text{D.E.} = \frac{\text{Average Weight (µg) recovered - Blank (µg)}}{\text{Weight (µg) added}}$$

The desorption efficiency may be dependent on the amount of nitroethane collected on the resin. Plot the desorption efficiency versus weight of nitroethane found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of µg per 2.0 ml since the samples are desorbed in 2.0 ml of ethyl acetate. The density of the analyte is used to convert milligrams into microliters for easy measurement with a microliter syringe. A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples in order to minimize variations in FID response. A calibration curve is established by plotting peak area versus concentration in µg per 2.0 ml.

For the internal standard method, use ethyl acetate containing a predetermined amount of the internal standard. The internal standard concentration used for these studies was approximately 70% of the analyte concentration for a standard solution representing a 3-liter collection at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in µg per 2.0 ml.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg per 2.0 ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample:

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample vial
µg blank = µg found in blank vial

10.3 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the weight of the analyte found in the front section of the tube by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

A similar procedure is followed for the backup (300 mg) section.

10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{75.07} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
75.07 = molecular weight of nitroethane
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Nitroethane, No. S219, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S219
January 20, 1978

Substance

Nitroethane

Standard

8-hour time-weighted average: 100 ppm (310 mg/cu m)

Analytical Method

A known volume of air is drawn through two XAD-2 tubes connected in series to trap the nitroethane vapors present. The nitroethane is desorbed from the XAD-2 with ethyl acetate, and the sample is analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 147.4-604 mg/cu m for a 3-liter sample at 22°C and 777 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The equipment needed for sampling nitroethane includes a calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at a flow rate between 0.03 and 0.05 liter per minute and an XAD-2 sampling tube series. The pump is calibrated with a representative sampling tube series in line.

The sampling tube series consists of two separate XAD-2 tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with a 10-mm O.D. and a 8-mm I.D. Each tube contains the appropriate amount of 20/50 mesh XAD-2. The XAD-2 must be prewashed with ethyl acetate and dried. The front tube contains 600 mg of XAD-2; the backup tube, 300 mg. A plug of silylated glass wool is placed at each end of the sorbent tube. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

Note that this sampling tube scheme is necessary to prevent sample migration upon storage.

Sample Size

A sample size of 3 liters is recommended. Sample at a known flow rate between 0.03 and 0.05 liter per minute.

Sampling Procedure

1. Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes (4-mm). Connect the front 600-mg tube to the 300-mg backup tube with a short piece of tubing.

2. The tube containing the 300 mg of XAD-2 is used as a backup and should be positioned nearest the sampling pump. The XAD-2 tube series should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the front XAD-2 tube.

4. A low flow rate pump is used. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate, and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. Immediately after sampling, the two XAD-2 tubes must be separated and each tube capped with the supplied plastic caps. The tubes should be identified to distinguish each corresponding pair of front and backup sampling tubes.

6. One set of XAD-2 tubes (a 600-mg tube and a 300-mg backup tube) should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This set of tubes should be labeled as a blank. Submit one blank for every ten samples.

7. Unused XAD-2 tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency may vary from one batch of XAD-2 to another. Record the batch number of the XAD-2 used.

Special Considerations

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Due to the high flow resistance of the XAD-2 tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without first fully recharging the battery.

Shipping Instructions

Capped XAD-2 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

Reference

Nitroethane, NIOSH Method No. S219.

Backup Data Report No. S219
January 20, 1978

Substance: Nitroethane

OSHA Standard: 100 ppm (310 mg/cu m)

Chemical Used for Validation: Nitroethane, 99%, Aldrich Chemical Company

General Considerations

The method for nitroethane has been tested in accordance with the various criteria for validation described in Reference 1, and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ±10% and the $\overline{CV}_T$ of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for nitroethane consisted of the following experimental studies:

- Determination of the breakthrough capacity of XAD-2 resin at high relative humidity,
- Analysis of a total of eighteen samples (six samples at each of the three test levels--0.5, 1, and 2X the OSHA standard) spiked with the appropriate amount of nitroethane to represent a sample volume equal to 3 liters,
- Analysis of a total of eighteen samples collected from dynamically generated test atmospheres (six samples at each of the three test levels--0.5, 1, and 2X the OSHA standard) for the same sample volume as above,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Development of Analytical Method

The method recommended for the sampling and analysis of nitroethane involves the use of an XAD-2 resin prewashed in ethyl acetate. Prewashed

XAD-2 was examined because studies with nitroethane gave inconsistent results with both analytical and collected samples prepared on 600 mg of unwashed XAD-2 and stored for seven days. These inconsistencies were not observed when similar tests were conducted on XAD-2 prewashed with ethyl acetate.

An experiment was conducted to determine if the inconsistencies noted above were indeed due to prewashing the resin or were only due to batch-to-batch resin variation. Comparisons of desorption efficiency, recovery and storage stability were made between two different batches of XAD-2, unwashed (Batch A and B), and prewashed with ethyl acetate (Batch AW and BW). Six samples were collected at the OSHA standard level simultaneously on each of the four sorbents. Similarly, 24 analytical spikes were prepared. Each set, or batch, was split such that three spikes and three samples were analyzed after one day and three spikes and three samples were stored and analyzed after seven days. The results are shown in Tables S219-1, S219-2, and S219-3 for the analytical spikes, the generated samples on unwashed XAD-2, and the generated samples on prewashed XAD-2 respectively.

Based on these results, only XAD-2 prewashed with ethyl acetate is recommended for the sampling and analysis of nitroethane. Although a particular batch of XAD-2 may prove satisfactory, observed inconsistencies in storage stability from batch to batch without the ethyl acetate prewash necessitate this procedure.

Principle of the Method

The method validated for the analysis of nitroethane in air is based on collection on XAD-2 resin, desorption with ethyl acetate, and analysis of the resulting solution by gas chromatography with a flame ionization detector. A sample size of 3 liters is recommended.

Analysis

The details of the equipment and instruments used for the analysis and the general approach used are described in Attachment A.

A detailed description of the procedure for analysis, the preparation of analytical samples for determination of desorption efficiency and the preparation of calibration standards are given in NIOSH Method No. S219 (Reference 3).

The reliability of the analytical method was tested based on the analysis of eighteen analytical samples. These samples were prepared by spiking 600 mg of XAD-2 with known aliquots of nitroethane representing the equivalent of a 3-liter air sample at 0.5, 1 and 2X the OSHA standard.

The data for the full set of eighteen analytical samples are shown in Table S219-4.

Table S219-1

Data Sheet: Nitroethane

Comparison of Four XAD-2 Resins: Analytical Spikes

Experiment A: Samples Stored One Day

BATCH A			BATCH B			BATCH AW			BATCH BW		
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
940	920	0.979	940	909	0.967	940	883	0.939	940	856	0.911
940	910	0.968	940	910	0.968	940	833	0.886	940	885	0.941
940	910	0.968	940	908	0.966	940	878	0.934	940	865	0.920
	mean	0.972		mean	0.967		mean	0.920		mean	0.924
	CV_1	0.00653		CV_1	0.001034		CV_1	0.0318		CV_1	0.01666

Experiment B: Samples Stored Seven Days

940	836	0.889	940	874	0.930	940	790	0.840	940	884	0.940
940	863	0.918	940	882	0.938	940	805	0.856	940	863	0.918
940	857	0.912	940	876	0.932	940	836	0.889	940	879	0.935
	mean	0.906		mean	0.933		mean	0.862		mean	0.931
	CV_1	0.01690		CV_1	0.00446		CV_1	0.02899		CV_1	0.01238
		6.8% loss			3.5% loss			6.3% loss			0.8% gain

Table S219-2

Data Sheet: Nitroethane

Comparison of Four XAD-2 Resins: Collected Samples on Unwashed XAD-2

Experiment A: Samples Stored One Day

BATCH A						BATCH B					
Found				Taken		Found				Taken	
µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
1003	1032	3.77	273.7	332		1243	1285	4.05	317	332	
1176	1210	3.89	311	332		1225	1267	3.94	322	332	
1244	1280	4.06	315	332		1105	1143	3.90	293.1	332	
		mean	299.9		0.903			mean	311		0.937
		CV_2	0.0760					CV_2	0.0497		

Experiment B: Samples Stored Seven Days

909	935	3.32	281.6	332		935	967	3.86	250.5	332	
1350	1389	4.28	325	332		1066	1102	3.89	283.3	332	
1029	1059	3.83	276.5	332		1005	1039	3.94	263.7	332	
		mean	294.4		0.887			mean	265.8		0.801
		CV_2	0.0905					CV_2	0.0621		
					1.8% loss						14.5% loss

[Δ] Corrected for one-day DE factor

S219-4

3095

Table S219-3

Data Sheet: Nitroethane

Comparison of Four XAD-2 Resins: Collected Samples on XAD-2 Washed with Ethyl Acetate

Experiment A: Samples Stored One Day

BATCH AW						BATCH BW					
Found				Taken		Found				Taken	
µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
1078	1172	3.95	296.7	332		1281	1386	4.06	341	332	
818	889	2.91	305	332		1309	1417	4.06	349	332	
864	939	2.98	315	332		1191	1289	3.77	342	332	
		mean	306		0.922			mean	344		1.036
		CV_2	0.02993					CV_2	0.01267		

Experiment B: Samples Stored Seven Days

1315	1429	4.17	343	332		1179	1276	3.89	328	332	
1099	1195	3.95	303	332		1206	1305	3.89	335	332	
1050	1141	3.89	293.3	332		1240	1342	3.77	356	332	
		mean	313		0.943			mean	340		1.024
		CV_2	0.0842					CV_2	0.0429		
					2.3% gain						1.2% loss

[Δ] Corrected for one-day DE factor

Table S219-4

Data Sheet: Nitroethane

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
470	416	0.885	940	790	0.840	1881	1666	0.886
470	415	0.883	940	819	0.871	1881	1668	0.887
470	427	0.909	940	804	0.855	1881	1575	0.837
470	407	0.866	940	819	0.871	1881	1672	0.889
470	436	0.928	940	820	0.872	1881	1656	0.880
470	412	0.877	940	811	0.863	1881	1688	0.897
n =		6			6			6
mean		0.891			0.862			0.879
std dev		0.02286			0.01262			0.02145
CV_1		0.02566			0.01464			0.02440

$\overline{CV}_1$ 0.02212

$\overline{CV}_{A+\overline{DE}}$ 0.02389

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachment B. A steady stream of nitroethane was delivered via a calibrated syringe drive at a rate of 66.3 mg/min to a dry air stream flowing at a rate of 0.1128 cu m/min. The three sample lines were maintained at measured dilution ratios of 0.244, 0.520 and 1.000 to produce test levels 0.5, 1, and 2X the OSHA standard. The delivery rate of the nitroethane was determined by calibrating the syringe drive as described in Attachment C. The data are shown in the section on Independent Method of Verifying Generator Concentration.

The samples were collected as described in NIOSH Method No. S219 using tubes packed with 600 mg of XAD-2. After initial cleaning, this resin must be washed with ethyl acetate and dried. Twenty-four samples were collected simultaneously at 0.05 liter per minute for 60 minutes (3 liters). Eighteen samples, six at each of the three test levels, were analyzed after one day, as described in Section 8.4 of NIOSH Method No. S219. The backup tubes collected at 2X the OSHA standard level were analyzed similarly. The six remaining samples were stored and analyzed after seven days.

The data obtained for the eighteen one-day-old samples are shown in Table S219-5.

Storage Stability and Migration Studies

Studies were done to assess the stability of nitroethane samples upon storage for one week at atmospheric conditions. For these studies, six samples collected at the OSHA standard level were stored for seven days and analyzed and the results compared with the data for six samples collected at the OSHA standard and analyzed after one day. The data for these samples, given in Table S219-6, show that the samples are stable over a seven-day period; the average recovery was 97.8% for the one-day-old samples vs. 103.8% for the seven-day-old samples.

In a separate experiment, migration studies were conducted by analyzing backup sections removed immediately after collection and comparing these results to tubes with the front and backup sections stored intact for seven days. Nitroethane was found in the backup sections of the tubes stored intact. The XAD-2 tube series described in NIOSH Method No. S219 is therefore recommended for sampling nitroethane vapors.

Breakthrough Tests

Breakthrough tests were done in an atmosphere where the relative humidity was 90%. Breakthrough is defined as the time at which the effluent concentration from the collection tube (containing 600 mg of XAD-2) is 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

Table S219-5

Data Sheet: Nitroethane
Sampling and Analysis

Test Level	Found				Taken	
	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	468	534	3.74	142.8	147.4	
	451	514	3.79	135.6	147.4	
	504	575	4.03	142.7	147.4	
	529	603	4.14	145.7	147.4	
	527	601	4.14	145.2	147.4	
	481	548	3.74	146.5	147.4	
			n = 6			
			mean	143.1		0.971
			std dev	3.98		
			CV_2	0.02781		
1S	1108	1263	4.03	313	314	
	1102	1257	3.91	321	314	
	1113	1269	3.97	320	314	
	997	1137	3.85	295.3	314	
	993	1132	3.85	294.0	314	
	1032	1177	3.91	301	314	
			n = 6			
			mean	307		0.978
			std dev	12.18		
			CV_2	0.0397		
2S	709	808	3.74	216.0*	604	
	2065	2355	3.74	630	604	
	2006	2287	3.74	611	604	
	2033	2318	3.85	602	604	
	2013	2295	3.85	596	604	
	2074	2365	3.74	632	604	
			n = 5			
			mean	614		1.017
			std dev	16.25		
			CV_2	0.02647		
			$\overline{CV}_2$	0.0322		

[Δ]Corrected for DE factor

*This value excluded from statistical analysis based on the Grubb's outlier test as described in Reference 2.

Table S219-6

Data Sheet: Nitroethane

Storage Stability of Collected Samples

Experiment A: Samples Stored One Day

Test Level

	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
1S	1108	1263	4.03	313	314	
	1102	1257	3.91	321	314	
	1113	1269	3.97	320	314	
	997	1137	3.85	295.3	314	
	993	1132	3.85	294.0	314	
	1032	1177	3.91	301	314	
			mean	307		0.978
			CV_2	0.0397		

Experiment B: Samples Stored Seven Days

1S	1143	1303	3.91	333	314	
	1154	1316	3.79	347	314	
	1069	1219	3.79	322	314	
	1194	1361	4.03	338	314	
	1111	1267	3.97	319	314	
	1010	1152	3.85	299.2	314	
			mean	326		1.038
			CV_2	0.0516		

[Δ]Corrected for DE factor

sample, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

The procedures for determining breakthrough in high relative humidity atmospheres together with the description of the equipment used are described in the section on Breakthrough Studies in Attachment B.

The time in minutes, the equivalent sample volume, and the mg collected on the resin when 5% breakthrough occurred at the test concentration used are summarized below.

Data for 5% Breakthrough at 90% Relative Humidity

Test Conc. (mg/cu m)	Flow Rate (liter/min)	Breakthrough time (min)	Volume (liters)	mg Collected at 5% Breakthrough
585	0.049	98	4.8	2.796

These tests were conducted at an atmospheric temperature of 22°C and an atmospheric pressure of 776 mm Hg. A 3-liter maximum sample size is recommended for nitroethane. This sample size will yield 1.86 mg of nitroethane at 2X the OSHA standard level (200 ppm or 620 mg/cu m) at 25°C and 760 mm Hg.

Independent Method of Verifying Generator Concentration

The method used for the independent determination of generator concentration was based on experimentally determining the delivery rate of nitroethane (in mg/min) into a measured dilution air flow (in cu m/min). On the basis of these two determined values, the Taken generator concentration at the 2S line can be calculated. The concentration at the 0.5S and 1S line can be calculated by measuring the dilution ratio of the 0.5S and 1S line relative to the 2S (main) line.

For the nitroethane generation, the syringe delivery rate was calibrated as described in the calibration section in Attachment C. The data, expressed in mg per minute for the replicate determinations, are indicated below.

65.8
65.4
65.8
67.2
66.5
66.9

Average = 66.3 mg/min

The corrected main line air flow was determined to be 0.1098 cu m/min at the respective atmospheric temperature and pressure conditions of 22°C and 777 mm Hg for this generation experiment. In addition, the sample lines were measured to have dilution ratios of 0.244, 0.520 and 1.000 to produce test levels at 0.5, 1 and 2X the OSHA standard.

Based on these data, the Taken generator concentration at the 0.5, 1 and 2S lines are respectively: 147.4, 314 and 604 mg/cu m.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2, and the data in Tables S219-4 and S219-5.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1 and 2X the OSHA standard for nitroethane generated samples. The data (Table S219-5) gave a chi squared value of 0.91 indicating that it is feasible to pool the coefficients of variation. Thus, CV_T is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$$\overline{CV}_1 = 0.02212 \qquad \overline{CV}_2 = 0.0322 \qquad \overline{CV}_T = 0.0602$$

The accuracy of the method was determined by comparison of the average value found by analysis of six samples at each of the three test levels with the Taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 98.9%.

Test Level	mg/cu m		Agreement (Found ÷ Taken)
	Taken	Found	
0.5S	147.4	143.1	97.1
1S	314	307	97.8
2S	604	614	101.7
		Average ...	98.9

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and storage stability tests, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

3. Nitroethane, NIOSH Method No. S219, prepared under NIOSH Contract No. 210-76-0123, with validation date January 20, 1978.

ATTACHMENT A

GAS CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the gas chromatography (GC) methods consists of a Varian 2700 Series Gas Chromatograph, a Varian Model 8000 automatic sample injector and a Spectra Physics System 1 computing integrator.

The Varian 2700 is a dual column unit equipped with a flame ionization detector and a photoionization detector (Hnu Systems, Inc.). The unit can be set for isothermal or for linear temperature program operation, either manually or automatically.

The Model 8000 automatic sample injector is mounted horizontally on the Varian 2700 and can readily be moved to align with either of the two injection ports. 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 dry nitrogen, and a control unit which permits total automation in a closed loop form with a computer. For this program, the syringe injector has been set to deliver 5 microliters of sample solution. The unit has been tested to verify that sample to sample cross-contamination does not occur and that the reproducibility of the sample injection is adequate. Periodic checks have been carried out on six or twelve repetitive injections of a standard solution in carbon disulfide and the observed standard deviation of the integrated peak areas is never greater than 2.5%.

All peak area measurements were done with the System 1 computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System 1 also has the capability to calculate sample concentration directly once the calibration factor has been determined.

Approach

The internal standard method (relative area measurements) has been used for this program not only because of its inherently better reproducibility than the external standard method (absolute area measurements) but also as a safeguard against any problems that could arise during the periods of unattended overnight operation. Such problems include detector response variations and the partial clogging of the sample injector loop which can give rise to variability in sample size injections. These clogging effects are caused by the very fine solid sorbent particles which remain suspended in the solution.

A comparative study of the reproducibility of the absolute area and the relative area measurements was performed using sec-butyl acetate (1.5 mg/ml) and undecane as internal standard. The precision of 12 successive determinations was 1.7% based on absolute areas and 0.4% using relative areas.

The choice of an internal standard has been restricted to those compounds which present minimal adsorption losses on the specific solid sorbent used. Experiments have been run to verify adsorption losses by determining the integrated areas of analyte and internal standard in a calibration solution and comparing these areas with the respective areas obtained when 1.0 ml (or other appropriate volume) aliquots of the same calibration solution are added to the appropriate amounts of solid sorbent. (Use the same weight of solid sorbent as that used for sampling.) The ideal internal standard is one which does not show any significant decrease in area due to the solid sorbent addition; this phenomenon is dependent on the interactive characteristics of the internal standard, the solid sorbent and the desorption solvent.

ATTACHMENT B

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S219-B-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 sampling devices are connected in parallel to the 0.5S dilution line and six to the 2S dilution line; twelve sampling devices are connected to the 1S dilution line. All these devices are connected via critical flow orifices (CFO's) to the 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, 0.017 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) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

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

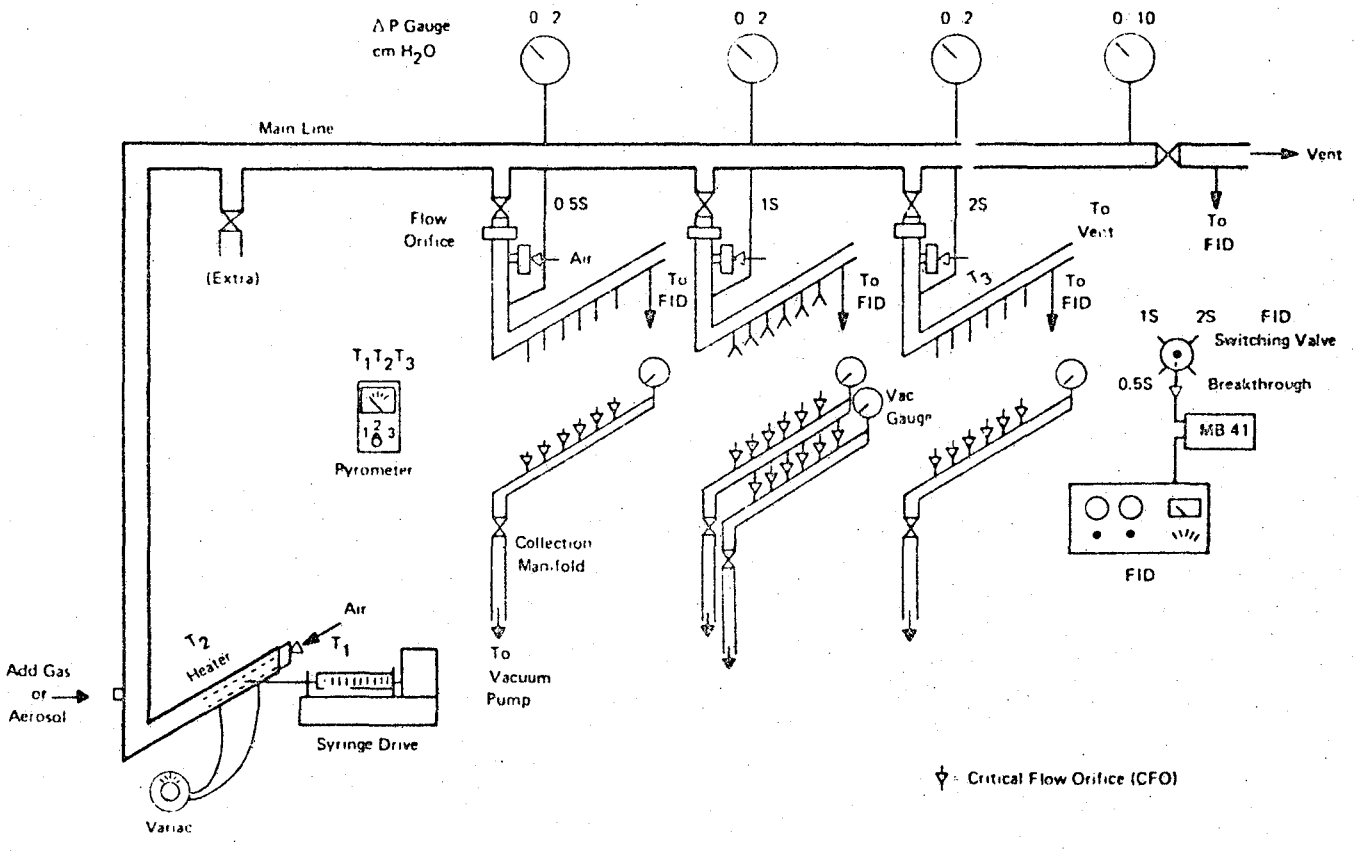


Figure S219-B-1. Vapor Generation/Dilution/Sampling System

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 sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. 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 a 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 (1.5 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

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 0.1128 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.

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	0.499	0.227

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

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. 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. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) 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.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S219-B-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.

2. Sample delivery rate is determined by appropriate calibration.

3. Sample is fed into Main Line until vapor concentration equilibrium is established.

4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.

5. The four sets of six samples from the three concentration levels are collected simultaneously.

Figure S219-B-2. Generation of High Humidity Atmospheres

ATTACHMENT C

VAPOR GENERATION

Continuous Direct Injection

Vapor concentrations from liquids are generated by adding known amounts of liquid to the Main Line of the vapor dilution/sampling apparatus. A continuous delivery rate is achieved using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25 G stainless steel needle in the Main Line by a short length of 0.16-cm (1/16-in) O.D. Teflon tubing. If the substance of interest is reactive with the stainless steel needle then the Teflon tubing is placed within the Main Line replacing the needle. When dealing with liquids of low volatility the 25G needle is mounted such that the tip of the needle rests inside a 10-cm length of 8-mm I.D. 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.

Calibration of Syringe Delivery

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 25-800 mg are collected depending on the specific compound being studied.

Calculation of Main Line 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.