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TEN NIOSH ANALYTICAL METHODS. SET-2

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Ten NIOSH Analytical Methods Set-2

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 requiring 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 not 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 2

Allyl glycidyl ether
Benzoyl peroxide
Chlorodiphenyl, 42% chlorine
Furfuryl alcohol
Hydroquinone
Iron oxide fume
Methylcyclohexanone
Methyl chloride
Stibine
Vanadium, V_2O_5 fume

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
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Allyl Glycidyl Ether

Analyte:	Allyl Glycidyl Ether	Method No.:	S346
Matrix:	Air	Range:	19-87 mg/cu m
OSHA Standard:	10 ppm (45 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.057
Procedure:	Adsorption on Tenax-GC desorption with ether, GC/FID	Validation Date:	1/21/77

1. Principle of the Method

1.1 A known volume of air is drawn through a Tenax-GC tube to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

1.2 The Tenax-GC in each tube is transferred to a vial and the allyl glycidyl ether is desorbed with diethyl ether and analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 19-87 mg/cu m at an atmospheric temperature of 17°C and atmospheric pressure of 752 mm Hg using a 3-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at 90% relative humidity when sampling a test atmosphere at 2X 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 upper limit of the range of the method is dependent on the adsorptive capacity of the Tenax-GC resin tube. This capacity can vary with the concentrations of analyte 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 of 19-87 mg/cu m was 0.057. This value corresponds to a 2.6 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 0.5% 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.

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 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 92 mg/cu m of allyl glycidyl ether was sampled at 0.8 liter per minute, 5% breakthrough was observed after 15 minutes (capacity = 12 liters or 1.1 mg). The sample size recommended is two-thirds the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard to minimize the probability of overloading the sampling tube and allow sampling with the 0.2 lpm sampling pump.

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 cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate of 0.2 liters per minute (Reference 11.3).

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6.2 Resin tubes. Glass tube with both ends flame-sealed, 10-cm long with 8-mm O.D. and 6-mm I.D., containing 2 sections of 35/60 mesh Tenax-GC 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.

6.3 Gas chromatograph with a flame ionization detector.

6.4 Column, (20-ft x 1/8 in. stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Sample containers with Teflon-lined caps, 5-ml.

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

6.8 Pipettes. 2-ml, delivery type.

6.9 Volumetric flasks. 1- and 10-ml or convenient sizes for making standard solutions and dilution of samples.

7. Reagents

7.1 Diethyl ether, anhydrous.

7.2 Allyl glycidyl ether, 99%.

7.3 Isoamyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in ether.

7.4 Hexane. This solvent is used to prepare the allyl glycidyl ether solutions for the desorption efficiency determination.

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 series in the line; the tube is described in Section 6.2. 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 two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (3 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 should 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 3 liters is recommended. Sample at a flow rate of 0.2 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 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.

8.4 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 5-ml screw-capped sample container. The separating section of glass wool is removed and discarded.

The second 50-mg section is transferred to another container. These two sections are analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 ml of ether is pipetted into each sample container. 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 internal standard solution in ether.

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. 280°C manifold temperature (detector)
6. 150°C column temperature

A retention time of approximately 10.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The internal standard elutes between ether and the allyl glycidyl ether.

8.4.4 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 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 Tenax-GC 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 the equivalent 1X 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 allyl glycidyl ether found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of allyl glycidyl ether found in the sample.

The analytical samples are prepared as follows: Tenax-GC, equivalent to the amount in the front section (100 mg), is measured into a 5-ml screw capped vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of allyl glycidyl ether 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.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5X, 1X and 2X of the OSHA standard) were prepared by adding an amount of allyl glycidyl ether equivalent to that present in a 3-liter sample at the selected level. A stock solution containing 67.34 milligrams of allyl glycidyl ether per milliliter of hexane was prepared. One, 2 and 4 microliter aliquots of the solution were added to the Tenax-GC resin 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 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 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 2.0 ml of ether 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.

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If the internal standard method is used, prepare calibration standards by using 2.0 ml of ether 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

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

The desorption efficiency may be dependent on the amount of allyl glycidyl ether collected on the resin. Plot the desorption efficiency versus weight of allyl glycidyl ether found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

9.1 Solutions of allyl glycidyl ether should be prepared over the appropriate concentration range in diethyl ether. The solutions should be prepared by addition of allyl glycidyl ether to 2.0 ml of diethyl ether in 5-ml vials. The allyl glycidyl ether may either be added neat using a microliter syringe or one may use the hexane solution described in Section 8.5.2. The concentration of standards can be expressed in terms of µg of allyl glycidyl ether per 2 ml of ether.

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 (ordinate) against sample concentration in µg/2.0 ml.

For the internal standard method, use ether 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 µg/2.0 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 2.0 ml ether 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 8.5.2) 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 = flow rate sampled

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.

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

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

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

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 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 Allyl Glycidyl Ether, No. S346, 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. S346

Substance

Allyl Glycidyl Ether

Standard

Ceiling: 10 ppm (45 mg/cu m)

Analytical Method

A known volume of air is drawn through a Tenax-GC resin tube to trap the allyl glycidyl ether vapors present. The allyl glycidyl ether is desorbed from the resin with diethyl ether, 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 19-87 mg/cu m for a 3-liter sample at 17°C and 752 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The sampling equipment needed consists of a Tenax-GC 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, ±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 flame sealed at both ends, 10-cm long with an 8-mm O.D. and a 6-mm I.D., packed with two sections of 35/60-mesh Tenax-GC 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 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 3 liters is recommended. Sample at a flow rate of 0.2 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 50 mg of resin is used as a backup and should be positioned nearest the sampling pump. The resin 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 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.

   In addition, three unused and sealed resin 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 of 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 per pump should be done without first fully recharging the battery.

3. The sample size recommended is less than two-thirds the breakthrough capacity at 90% relative humidity for a test atmosphere at a concentration twice the OSHA standard level. This breakthrough capacity was found to be 12 liters.

Shipping Instructions

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

Reference

Allyl Glycidyl Ether, NIOSH Method No. S346.

Backup Data Report No. S346

Substance: Allyl Glycidyl Ether

OSHA Standard: 10 ppm (45 mg/cu m) - Ceiling

Chemical Used for Validation: Allyl Glycidyl Ether, 99%, Aldrich Chemical Company

General Considerations

The method for allyl glycidyl ether 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 allyl glycidyl ether consisted of the following experimental studies:

- Evaluation of various solid sorbents relative to capacity and sample stability upon storage; the experimental studies on collected samples were supported by corresponding analytical method recovery studies,
- Analysis of a total of 18 samples (6 samples at each of the three test levels--0.5X, 1X and 2X the OSHA standard) spiked with the appropriate amount of allyl glycidyl ether 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--0.5X, 1X and 2X the OSHA standard) for the same sample volume as above,
- Determination of the breakthrough capacity of Tenax-GC resin at high relative humidities,
- 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.

Evaluation of Analytical Method and Solid Sorbents

The initial experiments conducted were based on the recommendations in the Allyl Glycidyl Ether Failure Report (Reference 3)--collection on Lot 105 activated charcoal, desorption with methylene chloride and analysis by GC-FID. The capacity of Lot 105 charcoal at high relative humidity (90%) was measured and the sample volume was established as 15 liters (1 liter per minute for 15 minutes). No breakthrough was observed when a test atmosphere at 90% RH and containing 87 mg/cu m was sampled at 0.19 liter per minute for 270 minutes.

Eighteen analytical samples were prepared by adding to 100-mg of Lot 105 charcoal an amount of allyl glycidyl ether equivalent to a 15-liter sample at 0.5, 1 and 2X the OSHA standard. The average desorption efficiency found was 99.7%. A dynamic test atmosphere was then generated and two sets of eighteen samples were collected on the same day--one set was analyzed after 1 day and the other set was analyzed after 7 days. The results of these studies showed a significant loss (30%) of allyl glycidyl ether upon storage as indicated by the data summarized in Table S346-1 (Set A). These data do not follow the storage stability trend exhibited by stored analytical samples as reported in Reference 3.

Subsequent studies were focused on finding a more suitable solid sorbent. Storage stability tests of samples collected on 100-mg of solid sorbents such as Tenax-GC, XAD-2, and Lot 104 charcoal were studied simultaneously. A set of 18 samples was collected simultaneously, and one of the solid sorbents was used to collect 6 samples at each of the three test concentrations. A 3-liter sample was collected (0.2 liter per minute for 15 minutes) and the tube capacity was assessed by analyzing the backup section. For each of the 3 sorbents studied, no allyl glycidyl ether was found in the backup sections. The data for these samples, also summarized in Table S346-1 (Set B) indicate that the collected allyl glycidyl ether was stable for 7 days on all three sorbents. Of these three sorbents, only Lot 104 charcoal and Tenax-GC were studied further. XAD-2 was ruled out because anomalous desorption efficiency values, ranging from 130-150%, were consistently observed. The average desorption efficiencies for Lot 104 charcoal and Tenax-GC ranged from 90-99%.

The capacity of both Lot 104 charcoal and Tenax-GC was determined at high relative humidity for test concentrations at 2X the OSHA standard. On the basis of these data, a capacity of at least 15 liters for Lot 104 charcoal and 3 liters for Tenax-GC was established. A set of 18 samples was collected on Lot 104 charcoal and another set was collected on Tenax-GC. Half of each set was analyzed after 1 day and the other half was stored for 7 days prior to analysis. The data in Table S346-1 (Sets C and D) show that only Tenax-GC favors sample stability over the three test levels. On Lot 104 charcoal, only the samples at the 2S test level appeared to be stable; this observation is in conflict with the Lot 104 charcoal data in Set B on the basis of total µg of allyl glycidyl ether collected on the charcoal, i.e., 3 liters at 2S showed no significant loss while 16 liters at 0.5S showed about a 17% loss.

Table S346-1

Storage Stability of Generated/Collected
Allyl Glycidyl Ether on Various Solid Sorbents

Sorbent/Solvent	Test Level	Sample Volume in liters	-mg/cu m Found*- Stored 1 day	Stored 7 days	Ratio (7 days:1 day)
Set A					
Lot 105/CH_2Cl_2	0.5S	16	19.16	13.83	0.722
	1S	16	41.5	26.93	0.649
	2S	16	91.3	62.6	0.686
Set B					
Tenax-GC/Ether$^{\Delta}$	0.5S	3	14.95	15.4	1.030
XAD-2/CH_2Cl_2	1S	3	34.5	34.9	1.012
Lot 104/CH_2Cl_2	2S	3	72.9	70.7	0.970
Set C					
Lot 104/CH_2Cl_2	0.5S	16	17.77	14.71	0.828
	1S	16	44.4	35.3	0.795
	2S	16	79.0	77.9	0.986
Set D					
Tenax-GC/Ether	0.5S	3	18.52	18.34	0.990
	1S	3	40.6	40.1	0.988
	2S	3	86.8	85.6	0.986

* The average values reported are based on the analysis of 3 samples except for the Lot 105/CH_2Cl_2 set which was based on 6 samples.

$^{\Delta}$ Ether was used because methylene chloride dissolves Tenax-GC.

Principle of the Method

The method validated for the analysis of allyl glycidyl ether in air is based on collection on Tenax-GC resin, desorption with ether, 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 the determination of desorption efficiency, and the preparation of calibration standards are given in NIOSH Method No. S346 (Reference 4).

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 Tenax-GC resin with known aliquots of allyl glycidyl ether in hexane. The aliquots (1, 2, 4 microliters) added contained respectively 67.3, 134.7, and 269.4 micrograms of allyl glycidyl ether 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 18 analytical samples are shown in Table S346-2.

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachment B. A steady stream of allyl glycidyl ether was delivered via a calibrated syringe drive at a rate of 9.27 mg/min to a dry air stream flowing at a rate of 0.1066 cu m/min. Due to the fairly high boiling point (154°C) of allyl glycidyl ether coupled with the use of cold air in the winter months when these studies were conducted, it was found necessary to vaporize the allyl glycidyl ether via the heated zone of the generator. (Refer to Figure 1, Attachment B.) Using this approach, a reproducible and steady stream of allyl glycidyl ether vapor was produced in the test chamber. The three sample lines were maintained at measured dilution ratios of 0.219, 0.483 and 1.000 to produce the 0.5X, 1X and 2X OSHA standard test levels. The delivery rate of the allyl glycidyl ether was determined by calibrating the syringe drive as described in Attachment B and the data are shown in the section on Independent Method of Verifying Generator Concentration.

The samples were collected using the tubes packed with 100 mg of Tenax-GC, 30/60 mesh, described in Section 6.2 of NIOSH Method No. S346. The eighteen samples, 6 at each of the three test levels, were collected simultaneously at 0.22 liter per minute for 15 minutes (3 liters). The samples were analyzed as described in Section 8.4 of NIOSH Method No. S346; the backup sections of the samples collected at 2X OSHA standard level were analyzed similarly.

Table S346-2

Data Sheet: Allyl Glycidyl Ether, No. S346
(Tenax-GC/100 mg, Samples Stored One Day)

Level	0.5S		1S			2S		
			Analysis					
µg added	µg found	DE	µg added	µg found	DE	µg added	µg found	DE
67.3	64.5	0.958	134.7	122.0	0.906	269.4	246.5	0.915
67.3	66.8	0.993	134.7	123.4	0.916	269.4	241.6	0.897
67.3	68.5	1.018	134.7	122.2	0.907	269.4	237.0	0.880
67.3	64.3	0.955	134.7	125.8	0.934	269.4	Sample Lost	
67.3	69.6	1.034	134.7	120.3	0.893	269.4	242.7	0.901
67.3	74.1	1.101	134.7	122.0	0.906	269.4	242.3	0.899
n =		6			6			5
mean		1.010			0.910			0.898
std dev		0.0547			0.01372			0.01248
CV_1		0.0541			0.01507			0.01389

$\overline{CV}_1 = 0.0344$

$\overline{CV}_{A+\overline{DE}} = 0.0372$

The data obtained for these 18 samples are shown in Table S346-3. It is also noted that no trace of allyl glycidyl ether was found in the backup sections of the tubes.

Storage Stability and Migration Studies

Studies were done to assess the stability of allyl glycidyl ether samples upon storage for one week at atmospheric conditions. For these studies, a set of 18 samples was collected and split into a set of 3 samples each at the three test levels. Nine samples were analyzed after 1 day and the results were compared with similar data obtained for the other nine samples stored for 7 days. The data for these samples given in Table S346-4 show that the samples are stable over a 7-day period; the average recovery was 98.1% for 1-day-old samples vs. 96.9% for 7-day-old samples.

Migration studies were conducted by analyzing backup sections removed immediately after collection and comparing these to backup sections stored intact for 7 days. Allyl glycidyl ether was not 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 100 mg of Tenax-GC) 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.

The time in minutes, the equivalent sample volume, and the mg collected on the resin when 5% breakthrough occurred at the test condition 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
92.3	0.793	15	11.90	1.098

These tests were conducted at an atmospheric temperature of 21°C, and an atmospheric pressure of 771 mm Hg. A 3-liter maximum sample size is recommended for allyl glycidyl ether. This sample size will yield 0.27 mg of allyl glycidyl ether at the 2X OSHA standard level, 20 ppm or 90 mg/cu m at 25°C and 760 mm Hg.

Table S346-3

Data Sheet: Allyl Glycidyl Ether, No. S346

Sampling and Analysis

(Tenax-GC/100 mg; Samples Stored 1 Day)

Test Level	Found				Taken	
	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	63.2	63.2	3.40	18.59	19.04	
	62.9	62.9	3.35	18.78	19.04	
	63.8	63.8	3.40	18.76	19.04	
	64.0	64.0	3.46	18.50	19.04	
	62.9	62.9	3.19	19.72	19.04	
	60.3	60.3	3.37	17.89	19.04	
			n = 6			
			mean	18.71		0.982
			std dev	0.593		
			CV_2	0.0317		
1S	129.9	142.8	3.32	43.0	42.0	
	126.2	138.7	3.38	41.0	42.0	
	126.4	138.9	3.37	41.2	42.0	
	127.9	140.6	3.50	40.2	42.0	
	129.3	142.1	3.32	42.8	42.0	
	132.0	145.0	3.41	42.5	42.0	
			n = 6			
			mean	41.8		0.995
			std dev	1.139		
			CV_2	0.0273		
2S	258.4	287.8	3.40	84.6	87.0	
	261.8	291.5	3.41	85.5	87.0	
	267.4	297.8	3.49	85.3	87.0	
	254.0	282.8	3.34	84.7	87.0	
	261.0	290.6	3.38	86.0	87.0	
	255.2	284.2	3.28	86.6	87.0	
			n = 6			
			mean	85.4		0.982
			std dev	0.766		
			CV_2	0.0090		
			$\overline{CV}_2$	0.0248		

Δ Corrected for DE factor

Table S346-4

Allyl Glycidyl Ether Storage Stability Test

Expt. A: Samples Stored 1 Day

Test Level	Found				Taken	
	µg	Corr µg[Δ]	Liters	mg/cu m	mg/cu m	Recovery
0.5S	62.6	62.6	3.40	18.41	19.01	
	65.2	65.2	3.36	19.40	19.01	
	60.4	60.4	3.40	17.76	19.01	
			Mean	18.52		0.974
			CV_2	0.0446		
1S	128.2	140.9	3.33	42.3	41.9	
	125.5	137.9	3.39	40.7	41.9	
	119.6	131.4	3.38	38.9	41.9	
			Mean	40.6		0.970
			CV_2	0.0419		
2S	262.6	292.4	3.40	86.0	86.8	
	267.0	297.3	3.42	86.9	86.8	
	274.8	306.0	3.50	87.4	86.8	
			Mean	86.8		1.000
			CV_2	0.00818		

Expt. B: Samples Stored 7 Days

0.5S	62.4	62.4	3.46	18.03	19.01	
	60.9	60.9	3.20	19.03	19.01	
	60.7	60.7	3.38	17.96	19.01	
			Mean	18.34		0.965
			CV_2	0.0325		
1S	121.6	133.6	3.51	38.1	41.9	
	123.8	136.0	3.33	40.8	41.9	
	128.8	141.5	3.42	41.4	41.9	
			Mean	40.1		0.957
			CV_2	0.0438		
2S	261.2	290.9	3.34	87.1	86.8	
	268.7	299.2	3.39	88.3	86.8	
	239.7	266.9	3.28	81.4	86.8	
			Mean	85.6		0.986
			CV_2	0.0431		

Δ Corrected for DE factor

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Independent Method of Verifying Generator Concentration

The method used for independent determination of generator concentration was based on experimentally determining the delivery rate of allyl glycidyl ether (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 allyl glycidyl ether 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.

9.102
9.085
9.180
9.298
9.433
9.524

Average = 9.270 mg/min

The corrected main line air flow was determined to be 0.1066 cu m/min at the respective atmospheric temperature and pressure conditions of 17°C and and 752 mm of Hg for this generation experiment. The dilution ratios for this test run were measured to be 0.219, 0.484 and 1.000 on the basis of relative total hydrocarbon readouts at the 0.5S, 1S and 2S test lines during sampling. These ratios were maintained to produce the 0.5, 1 and 2X OSHA standard test levels.

Based on these data, the Taken generator concentration at the 0.5S, 1S and 2S lines are respectively - 19.04, 42.0 and 87.0 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 Appendix C and the data in Tables S346-2 and S346-3.

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for allyl glycidyl ether. The data (Table S346-3) gave a chi squared value of 6.1, 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.

$\overline{CV}_1 = 0.0344$ $\overline{CV}_2 = 0.0248$ $\overline{CV}_T = 0.0573$

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 98.6%.

Test Level	mg/cu m		Agreement (Found ÷ Taken)
	Taken	Found	
0.5S	19.04	18.71	98.2
1S	42.0	41.8	99.5
2S	87.0	85.4	98.2
		Average --	98.6%

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 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 1/6/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

3. Failure Report on Allyl Glycidyl Ether, No. S346, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

4. Allyl Glycidyl Ether, NIOSH Method No. S346, prepared under NIOSH Contract No. 210-76-0123 with validation date 1/21/77.

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 Sc^3H electron capture detector. 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 Tenax-GC particles which remain suspended in the solution.

The choice of an internal standard has been restricted to those compounds which present minimal adsorption losses on Tenax-GC. 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 aliquots of the same calibration solution are added to 100 mg portions of Tenax-GC. The ideal internal standard is one which does not show any significant decrease in area due to the Tenax-GC addition.

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 S346-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 charcoal tubes are connected in parallel to each of the three dilution lines and are connected via critical flow orifices (CFO's) to the three corresponding vacuum lines.

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

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 cu m/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.017 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.

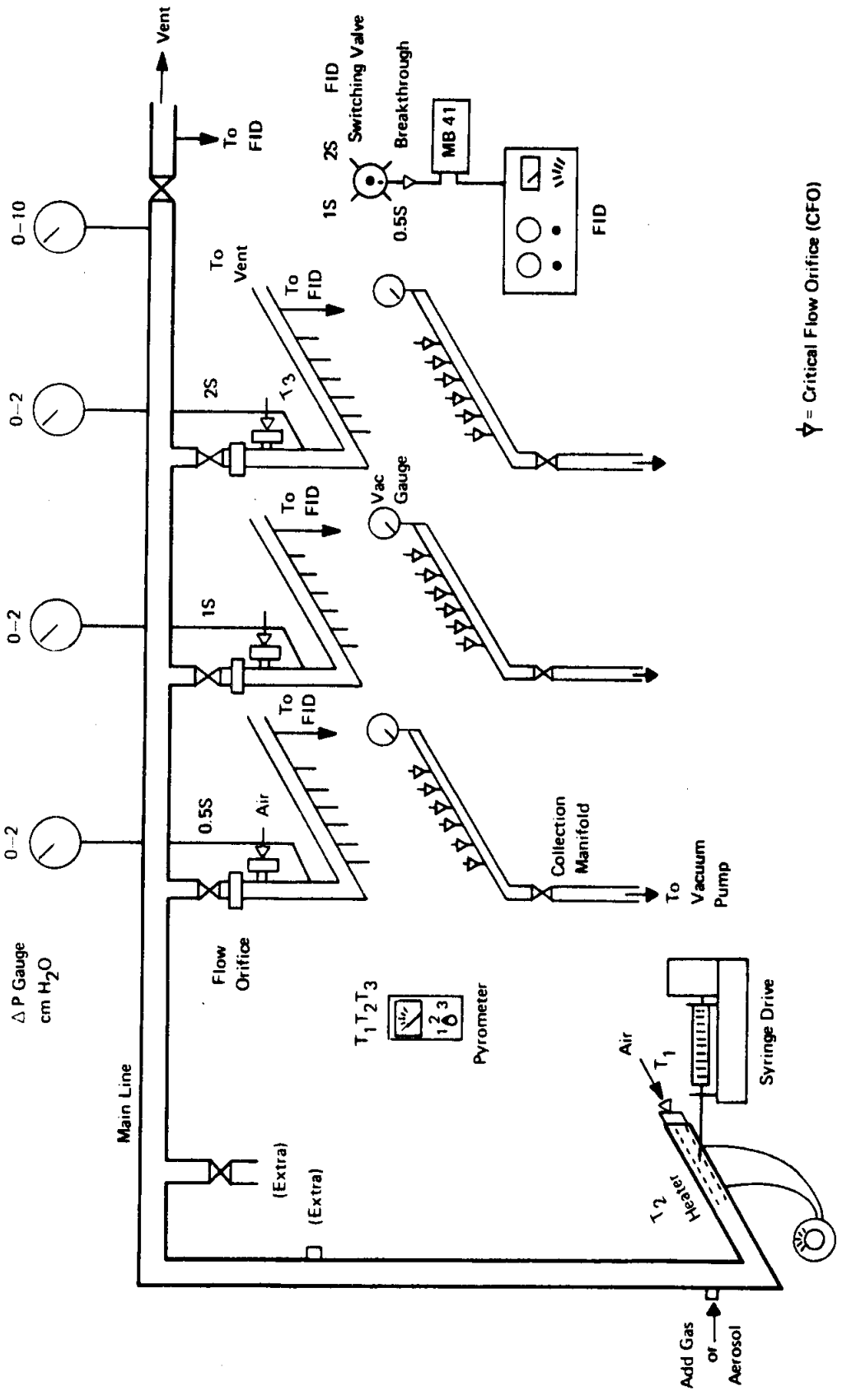


Figure S346-B-1 Vapor Generation/Dilution/Sampling System

- as a gas such as from a gas cylinder via an orifice or other flow controller,
- as a liquid via a syringe injector
- 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 is 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 S346-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 charcoal tubes connected to the dilution lines is established by connecting each of the tubes by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) OD vacuum manifold. Each dilution line has a separate manifold

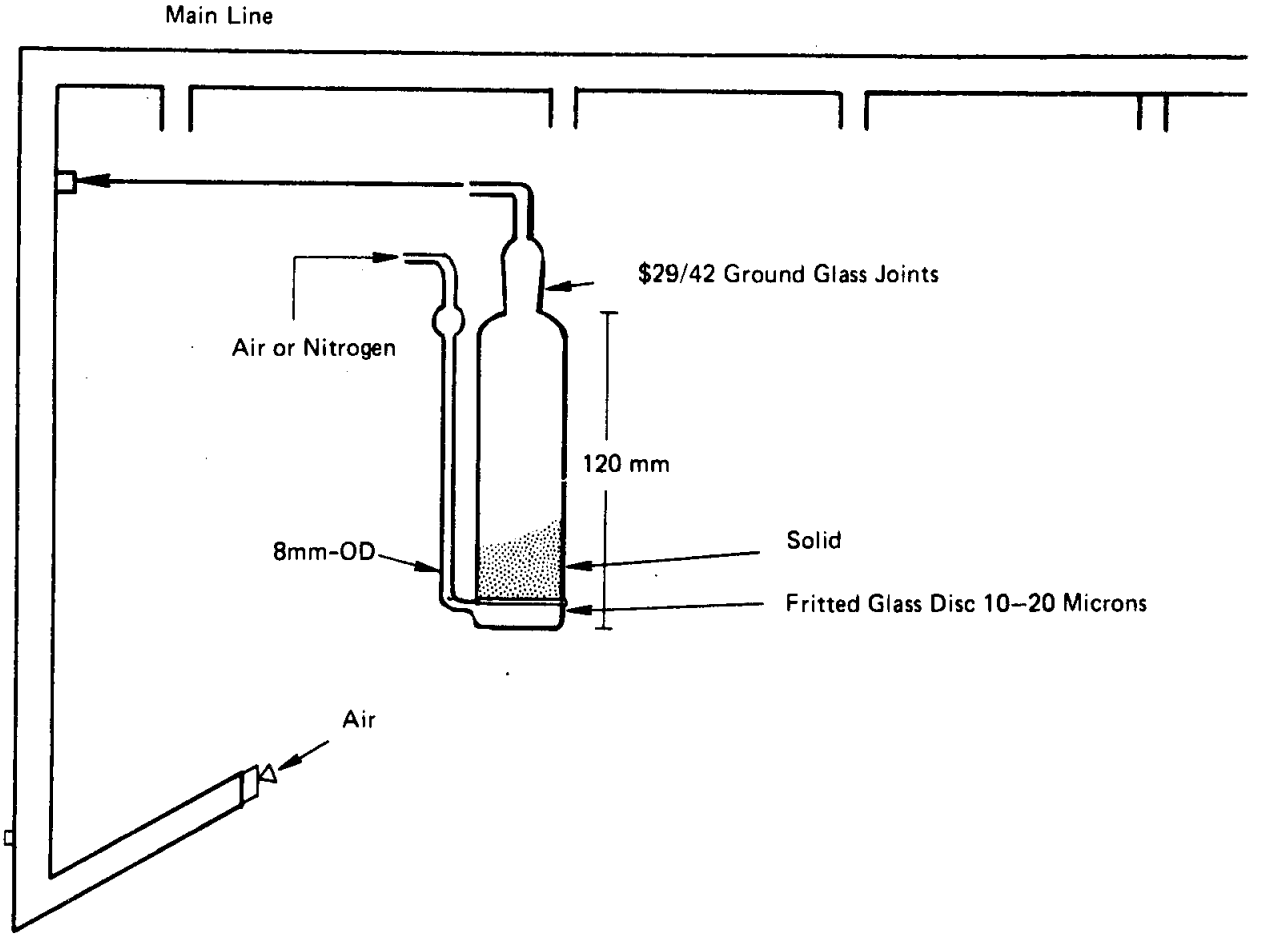


Figure S346-B-2 Vapor Generator for Solids

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.

Calculation of Vapor Concentration

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

Dilution Ratios

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

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

		Relative Concentration		
Case Generated	Main Line	2S	1S	0.5S
4X	1.000	0.5097	0.2557	0.1311
2X	1.000	1.000	0.4916	0.2384

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

Monitors

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

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

Breakthrough Studies

A. Low Relative Humidity (Dry Air)

For the measurement of charcoal tube capacity for a given vapor (breakthrough) six charcoal tubes containing only the 100 mg "front half" section of charcoal are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) OD stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp Model MB41 pump. Flow through the orifice was measured as 1.14 liters per minute providing a 0.19-liter per minute flow to each of the tubes. (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 S346-B-3. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 inch 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 six sets of samples from the three concentration levels are collected simultaneously.

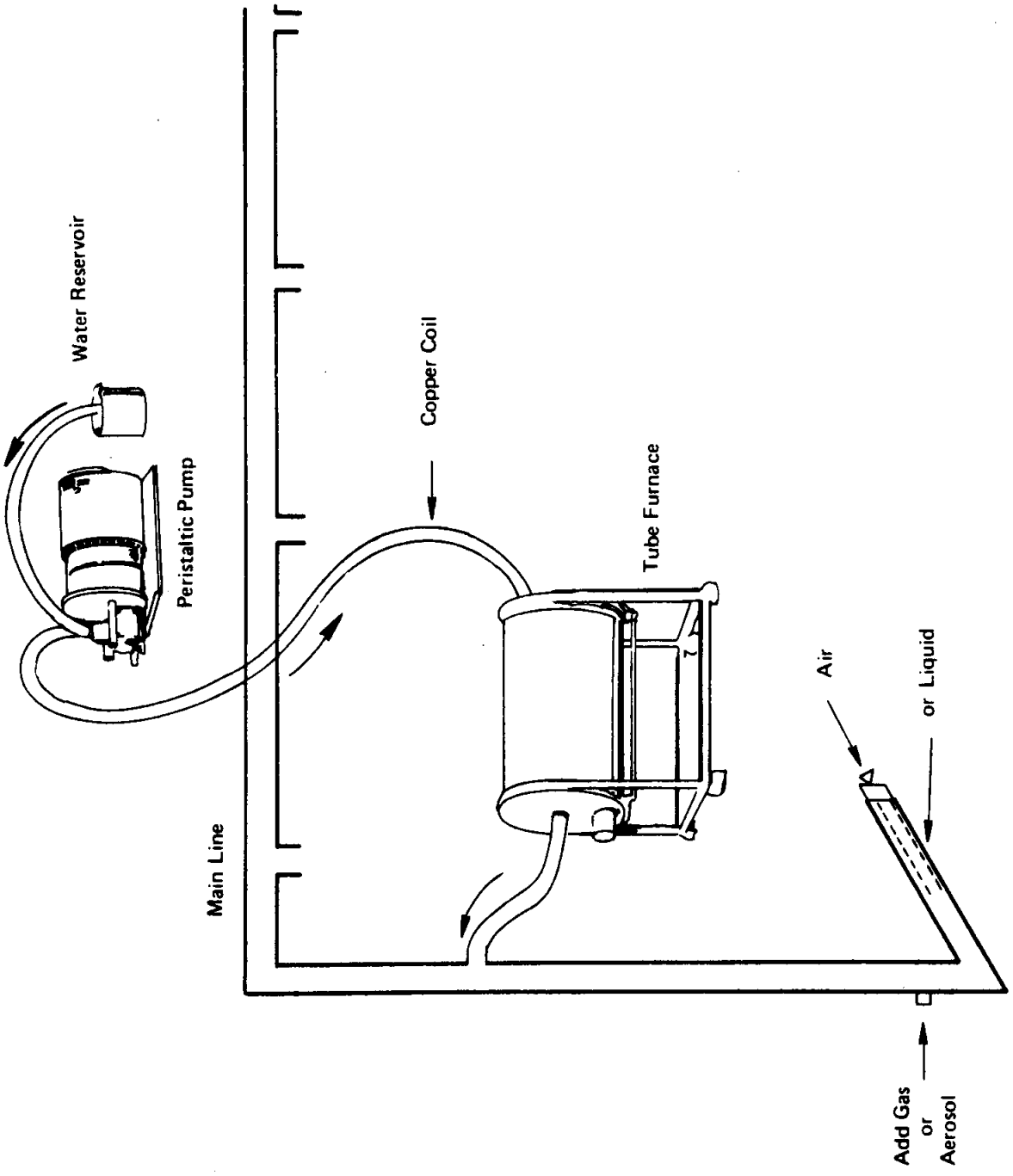


Figure S346-B-3 Generation of High Humidity Atmospheres

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.

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

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

Analyte:	Benzoyl Peroxide	Method No.:	S253
Matrix:	Air	Range:	3.12-19.10 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.060
Procedure:	Filter collection, ethyl ether extraction, HPLC	Validation Date:	1/21/77

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to collect benzoyl peroxide.

1.2 Benzoyl peroxide is extracted from the filter with ethyl ether, and the sample is analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 3.12-19.10 mg/cu m at an atmospheric temperature of 26°C and pressure of 764 mm Hg, using a 90-liter sample.

2.2 The upper limit of the range of the method depends on the capacity of the cellulose ester membrane filter. If higher concentrations than those tested are to be sampled, smaller volumes should be used. Higher volumes can also be used as long as particulate filter loading remains less than 2 mg.

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 benzoyl peroxide 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 3.12-19.10 mg/cu m was 0.060. This value corresponds to a standard deviation of 0.30 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 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. Storage stability studies on samples collected from a test atmosphere at a concentration of 7.30 mg/cu m indicate that after one week there is a 9.3% decrease in the amount of benzoyl peroxide recovered from the filter. In this study the filter samples were held in the filter cassettes at room temperature. Other tests show that benzoyl peroxide is stable in ethyl ether at room temperature for at least one week. Thus, there may be up to 9.3% loss of the analyte if the samples are not extracted immediately or refrigerated. Otherwise, the Coefficient of Variation is a good measure of the accuracy of the method, and no recovery correction should be applied to the final result in Section 10.5.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick instrumental method.

5.2 If samples are not returned to the laboratory promptly, there may be loss of material on the filter.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type MF or equivalent) with a pore size of 0.80 micrometer, and a 37-mm two-piece cassette filter holder supported by a cellulose pad.

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

6.3 Manometer.

6.4 Thermometer.

6.5 Scintillation Vials: 20 ml. The vial caps should be lined with Teflon for proper seal.

6.6 High performance liquid chromatograph equipped with a 254-nm fixed wavelength uv detector and a sample injection valve with a 20-microliter external sample loop. The injection valve is fitted with a syringe filter to remove filter fibers which 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, CA.

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

6.9 Tweezers.

6.10 Microliter Syringes: 10 and 100-microliter.

6.11 Volumetric Flasks: Convenient sizes for preparing standard solutions.

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

7. Reagents

7.1 Benzoyl peroxide, 99% pure.

7.2 Ethyl ether, purified, and containing no stabilizer.

7.3 Methanol, distilled in glass.

7.4 Water, deionized and distilled.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials 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 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 cellulose support pad. Secure the cassette holder together with tape or shrinkable band.

8.3.2 Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

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

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

8.3.5 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 rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and record ambient temperature and pressure, sample flow rate, and collection time. If pressure reading is not available, record the elevation.

8.3.7 Record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

8.3.9 The cassette filter holders in which the samples are stored 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

Upon receipt in the laboratory, the filters should te transferred to clean scintillation vials with clean tweezers and extracted with ether and the solutions stored in the refrigerator until they are analyzed. If it is not feasible to extract the filters immediately, the filters should be refrigerated as soon as possible. However, extractions should be done as soon as possible.

8.4.1 Each sample is analyzed separately.

8.4.2 Pipet 10 ml of ethyl ether into each scintillation vial.

8.4.3 Swirl the contents in each bottle.

8.4.4 Appropriate filter blanks must be analyzed at the same time as the samples.

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

Column Temperature: Ambient
Column Pressure: 1300 psi
Flow Rate: 1.6 ml/min
Mobile Phase: 70% methanol/30% water (V/V)
Detector: uv photometer at 254 nm
Range: 0.08 O.D.

8.4.6 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 the sample (100 microliters), and inject the sample.

8.4.7 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 benzoyl peroxide from the cellulose ester membrane filter. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for Determining Analytical Method Recovery. An appropriate aliquot of a 11.25 mg/ml solution of benzoyl peroxide in ethyl ether is added to a 37-mm MCEF filter. The amount added is equal to the amount of benzoyl peroxide collected in a 90-liter sample at 2X, 1X and 0.5X the OSHA standard level. Six spiked samples are prepared at each level along with six blanks. The samples are then analyzed according to the method in Section 8.4.

Analytical Method Recovery (A.M.R.) equals the weight in mg found on the filter divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg taken}}$$

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/10 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 11.25 mg/ml benzoyl peroxide stock standard solution by dissolving 281.25 mg benzoyl peroxide in ethyl ether and diluting to 25 ml in a volumetric flask. This solution should be stored in the refrigerator when not in use.

9.2 From the above stock solution, appropriate aliquots are withdrawn

and dilutions are made in ethyl ether. Prepare at least 5 working standards to cover the range of 0.045 mg-1.35 mg/10 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 benzoyl peroxide in mg/10 ml versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/10 ml of ethyl ether 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.

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

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Corrections for analytical method recovery (A.M.R.) must be made.

$$\text{Corrected mg/sample} = \frac{\text{mg (Section 10.2)}}{\text{A.M.R.}}$$

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 = 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)

10.5 The concentration of benzoyl peroxide in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000\ \text{(liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

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

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

Sampling Data Sheet No. S253

Substance

Benzoyl Peroxide

Standard

8-hour time-weighted average: 5 mg/cu m

Analytical Method

A known volume of air is drawn through a cellulose ester membrane filter to trap benzoyl peroxide. Benzoyl peroxide is extracted from the filter with ethyl ether, and the sample is separated and analyzed using a high pressure liquid chromatograph with a uv detector. The method has been validated over the range of 3.12-19.10 mg/cu m for a 90-liter sample at 26°C and 764 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 liter per minute, a 37-mm two-piece cassette filter held together by tape or shrinkable band, and a 37-mm/0.8-micrometer cellulose ester membrane filter supported by a cellulose backup pad.

Sample Size

A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liter per minute. Larger sample volumes can be collected provided sample loading does not exceed 2 mg.

Sampling Procedure

1. Assemble the filter and two-piece filter cassette and close firmly. Examine the holder for a good filter seal. The filter is supported by a cellulose backup pad. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with stretchable tape or a shrinkable band.

2. Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3. Air being sampled should not be passed 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 the flow rates readjusted as needed. If the flow rate cannot be adjusted to correct the problem, terminate sampling.

5. Record sample identity and all relevant sample data such as sample flow rate and collection time.

6. With each batch of ten samples, submit one filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

Special Considerations

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.

2. Upon receipt of the samples in the laboratory, the filters should be transferred to scintillation vials, extracted with ether, and the solutions stored in the refrigerator. If it is not feasible to extract the filters immediately, the filters should be refrigerated as soon as possible. The samples must be received by the laboratory within 5 days of collection.

Shipping Instructions

The cassette filter holders in which the samples are stored 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

Benzoyl Peroxide, NIOSH Method No. S253.

Backup Data Report

Substance: Benzoyl Peroxide, No. S253

OSHA Standard: 5 mg/cu m

Chemical Used for Validation: Benzoyl Peroxide, 99% pure
J. T. Baker Chemical Company

General

The procedure for collection and analysis of air samples of benzoyl peroxide is described in NIOSH Method No. S253. This method consists of collection of the sample on cellulose ester membrane filters, extraction with ethyl ether, and analysis of the resulting solution by high pressure liquid chromatography.

This method has been tested for validity 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 benzoyl peroxide 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 cellulose ester membrane filters.

Test the storage stability of six collected samples.

Test the storage stability of spiked samples in light and dark environments.

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. S253. The results of the analytical method recovery tests are in Table S253-12.

Sampling and Analysis

Samples of benzoyl peroxide in air were generated by the procedure described in Attachments A and B and collected as described in Method No. S253. The results of the sampling and analysis experiments are presented in Table S253-13.

A 0.5% solution of benzoyl peroxide in acetone was used in the aspiration system for the generation of benzoyl peroxide. To obtain the desired concentration, a set of generation conditions were chosen, and 15-minute samples 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 and 0.5X levels. Twelve samples were collected simultaneously at the 1X level, six of which were used for the storage stability test. The estimated average size of the particles was less than one micron diameter.

Samples were collected for 90 minutes at a flow rate of approximately 1.5 liter per minute.

Collection Efficiency

Collection efficiency tests were conducted at 19.10 mg/cu m (as determined by the method being tested) by mounting in series two filters in direct contact with each other. The results of the collection efficiency test are presented below:

Table S253-1: Collection Efficiency Tests

mg/cu m found first filter	mg/cu m found backup filter	Collection Efficiency
18.48	N.D.*	1.00
19.29	N.D.*	1.00
18.90	N.D.*	1.00
19.37	N.D.*	1.00
19.53	N.D.*	1.00
19.02	N.D.*	1.00
mean 19.10		
std dev 0.38		
CV 0.020		

*Not detected at a detection limit of 0.10 mg/cu m.

Storage Stability

A storage stability test was conducted to assess whether benzoyl peroxide could be successfully stored on a filter for one week after collection. Twelve samples were collected simultaneously at 1X the OSHA standard level. Six samples were analyzed immediately and the remaining six samples were stored in filter holders for one week before analysis. The

results of the storage stability test are presented below:

Table S253-2: Samples Stored on Filters in Filter Cassettes

Samples Analyzed Immediately mg/cu m	Samples Analyzed After One Week mg/cu m
7.74	6.91
7.08	6.93
7.13	6.73
7.17	6.50
7.39	6.00
	6.65
mean 7.30	6.62
std dev 0.27	0.34
CV 0.037	0.051

$$\text{Recovery} = \frac{\text{One Week}}{\text{Immediate}} = 0.907$$

A second storage stability test was conducted to assess whether benzoyl peroxide could be successfully stored in ethyl ether. Twelve vials containing 10 ml of ethyl ether were spiked with 40 microliters of a 11.25 mg/ml solution of benzoyl peroxide in ethyl ether. The amount spiked (0.450 mg) represents the amount of benzoyl peroxide present at 1X the OSHA standard level for a 90-liter air sample. Six of the samples were analyzed immediately, and the remaining six samples were stored for 18 days before analysis. The results are presented below:

Table S253-3: Samples Stored in Scintillation Vials in Ethyl Ether

Samples Analyzed Immediately (mg found)	Samples Analyzed After Storage for 18 Days in Ethyl Ether (mg found)
0.438	0.443
0.449	0.445
0.448	0.421
0.446	0.426
0.440	0.415
0.439	0.432
mean 0.443	0.430
std dev 0.005	0.012
CV 0.011	0.028

$$\text{Recovery} = \frac{\text{18 Days}}{\text{Immediate}} = 0.971$$

The storage stability studies indicate that benzoyl peroxide is sufficiently stable on the cellulose ester membrane filter for one week. Better recoveries were obtained when the samples were extracted with ethyl ether immediately after collection and stored in scintillation

vials. This procedure was not recommended, because shipment of ethyl ether through the U. S. mail is prohibited. Upon receipt of the samples in the laboratory, the filters should be extracted with ethyl ether and the solutions stored in the refrigerator until they are analyzed. If it is not feasible to extract the filters immediately, the scintillation vial containing the filter should be refrigerated as soon as possible.

A third storage stability study was conducted to determine if benzoyl peroxide is equally stable in light and dark storage environments. Twelve vials containing 10 ml of ethyl ether were spiked with 0.450 mg of benzoyl peroxide as described above and stored for ten days. Six vials were placed in a dark box and six vials were left on the laboratory bench near a window. The results of the analyses of these samples are presented below:

Table S253-4

Samples Stored in the Dark	Samples Stored in the Light
mg	mg
0.580*	0.413
0.404	0.434
0.428	0.524
0.426	0.508
0.428	0.424
0.434	0.451
mean 0.424	0.459
std dev 0.012	0.046
CV 0.028	0.100

*Not included in calculation, because this number is an outlier.

Under the above conditions, benzoyl peroxide is stable when stored in light.

A study was conducted to determine if benzoyl peroxide is equally stable in two types of ethyl ether which are available in the laboratory. The two ethers studied are:

1. Ethyl ether, anhydrous (contains a stabilizer, 0.000005% sodium diethyldithiocarbamate) from Mallinckrodt, #0848.

2. Ethyl ether, purified (contains no stabilizer) from Mallinckrodt, #0844.

Four vials containing 10 ml of anhydrous ethyl ether and four vials containing 10 ml of purified ethyl ether were spiked with 562 micrograms of benzoyl peroxide. The samples were analyzed immediately and after six

days. The results are presented below:

Table S253-5: Storage Stability of Benzoyl Peroxide in Anhydrous Ethyl Ether and Purified Ethyl Ether

		Samples Analyzed Immediately (micrograms)	Samples Analyzed After Six Days (micrograms)
Ethyl Ether, Anhydrous		600	552
		599	522
		557	546
		557	551
	mean	578	543
	std dev	25	14
	CV	0.043	0.026

$$\text{Recovery} = \frac{\text{Six Days}}{\text{Immediate}} = 0.939$$

Ethyl Ether, Purified		553	569
		524	568
		547	559
		558	535
	mean	545	558
	std dev	15	16
	CV	0.028	0.029

$$\text{Recovery} = \frac{\text{Six Days}}{\text{Immediate}} = 1.024$$

The results indicate that benzoyl peroxide may be more stable in the purified ether. Subsequent experimental work was done using the purified ethyl ether.

Discussion

The following preliminary experiment was conducted to determine if filter collection is appropriate for benzoyl peroxide. An assumption was made that benzoyl peroxide will be a particulate over the concentration range to be validated. A test atmosphere of benzoyl peroxide in air was generated at 6.97 mg/cu m. Six samples were collected on cellulose ester membrane filters followed by a midget bubbler charged with acetone. The filters were extracted with 10 ml of ethyl ether and analyzed by high pressure liquid chromatography. The contents of the bubblers were analyzed separately. The results are presented in Table S253-6.

Table S253-6: Collection Efficiency of Benzoyl Peroxide on MCE Filters

Amount of Benzoyl Peroxide Collected on Filter (mg/cu m)	Amount of Benzoyl Peroxide Collected in the Bubbler (mg/cu m)	Percent Collected on Filter
6.67	N.D.*	100.0%
6.80	N.D.*	100.0%
6.59	N.D.*	100.0%
7.71	N.D.*	100.0%
6.62	N.D.*	100.0%
7.40	N.D.*	100.0%
mean 6.97		
std dev 0.47		
CV 0.067		

*N.D. = Not detectable at a detection limit of 0.008 mg/cu m

The above results indicate that collection of benzoyl peroxide on cellulose ester membrane filters is satisfactory.

Since benzoyl peroxide is a reactive chemical, it was desired to verify that significant deterioration of the purchased benzoyl peroxide had not occurred. A measured quantity of benzoyl peroxide was reacted with iodide ions to form benzoic acid. This was then derivatized with diazomethane. (This method is described later in this report.) The amount of derivative formed was compared with standards prepared by derivatization of benzoic acid. Analysis was done by gas chromatography. The ratio of the amount of methyl benzoate formed from benzoyl peroxide to the amount of methyl benzoate formed from benzoic acid indicated that the benzoyl peroxide used was 99% pure, as stated by the manufacturer.

Method of Verifying the Concentration in the Sample Generator

An attempt was made to find an alternate method of measuring the concentration of benzoyl peroxide in the test atmosphere, so that a comparison could be made with the method being tested.

Early investigations explored the possibility of using an iodometric titration (Reference 2). The majority of organic peroxides are readily reduced by iodide ions in acid solution, reacting quantitatively:

$$ROOR + 2I^- + 2H_2O \longrightarrow I_2 + 2ROH + 2OH^-$$

The reaction must be carried out in the dark in the absence of oxygen since the following side reaction can occur:

$$4I^- + O_2 + 4H^+ \rightleftharpoons 2I_2 + 2H_2O$$

This equilibrium is accelerated by acid, heat, and light. After the iodide ions have reacted with the peroxide, the liberated iodine is titrated with standard sodium thiosulfate solution as follows:

$$2S_2O_3^{-2} + I_2 \longrightarrow S_4O_6^{-2} + 2I^-$$

After considerable surveying of the literature, a method described by Skellon and Wills (Reference 3) was chosen.

First attempts gave non-reproducible results and a high blank, probably due to dissolved oxygen in the water. Therefore, all solutions and dilutions were made with freshly boiled and cooled distilled water. The method is as follows:

> Spike Millipore MF-membrane filter with benzoyl peroxide and place in a 250-ml glass stoppered Erlenmeyer flask. Add 25 ml glacial acetic acid and 5 ml water. Add 2 g sodium bicarbonate and replace stopper after gas evolution slows. Place in the dark for 10 minutes and then add 2 ml sodium iodide solution (2 g in 10 ml water). Place in dark for 15 minutes. Dilute with 100 ml water and bubble nitrogen through solution throughout the titration. Titrate with 0.01 N sodium thiosulfate to a pale yellow color. Add 5 ml starch indicator solution and complete the titration to disappearance of blue color.

Three filters were spiked with 450 micrograms of benzoyl peroxide. The results are shown below:

Table S253-7

Sample Number	Volume of Titrant	Micrograms Benzoyl Peroxide
Blank	0.19 ml	--
1	0.56 ml	448
2	0.45 ml	315
3	0.66 ml	799
	mean	521
	std dev	250

The precision was unacceptable.

Another experiment was run at higher levels in an attempt to improve precision. Four filters were spiked with 3.60 mg of benzoyl peroxide, and these results are shown below.

Table S253-8

Sample Number	Volume of Titrant	mg of Benzoyl Peroxide
Blank	0	--
1	3.075 ml	3.72
2	3.090 ml	3.74
3	3.248 ml	3.93
4	3.210 ml	3.89
	mean	3.82
	std dev	0.11

In this case, the larger sample has improved precision, however, this method could not be used because it is not sensitive enough for the levels anticipated.

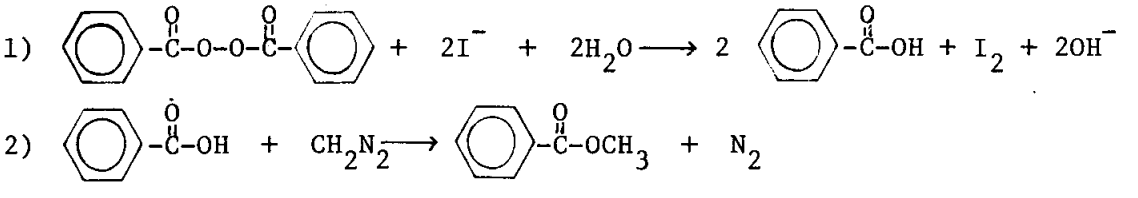
Another approach was to collect the benzoyl peroxide in midget impingers and determine the concentration by liquid chromatography. Acetone was used in a set of three impingers at the 2X level, and the resulting solutions were analyzed by liquid chromatography for benzoyl peroxide. The following results were obtained.

Table S253-9

Sample Number	Flow Rate (liters/min)	Volume Sampled (liters)	mg Benzoyl Peroxide	mg/cu m
1	2.247	145	1.02	7.03
2	2.273	146	1.04	7.12
3	2.292	148	1.01	6.82
			mean	6.99
			std dev	0.15

It is apparent that midget impingers cannot be used to collect benzoyl peroxide, since the average concentration at the 2X level was 19.10 mg/cu m. Therefore, only 36.6% of the benzoyl peroxide was collected in the midget impinger.

The final method chosen was conversion of benzoyl peroxide to methyl benzoate and analysis of the ester by gas chromatography. In this method, benzoyl peroxide is collected on a Millipore MF membrane filter, extracted with ether, reduced by potassium iodide solution, esterified by diazomethane, and the ester quantitated by gas chromatography.



According to Tabolsky and Mesrobian (Reference 4), Reaction 1 is quantitative. Diazomethane was chosen for a derivatization reagent because of its known quantitative reaction with benzoic acid. Benzoic acid is used as a titrant in the determination of diazomethane concentrations (Reference 5).

The following reagents and standards were prepared:

1. Potassium Iodide Reagent - saturated solution of potassium iodide in 2-propanol.

2. Diazomethane Reagent - prepared according to the method of Arndt (Reference 5). To 100 ml of ether, 30 ml of 40% KOH is added, and the mixture is cooled to 5°C. To this mixture, with continued cooling and shaking, 10 g of finely powdered nitrosomethylurea is added. The ether layer, which is the top layer, can be decanted readily. It contains some dissolved impurities and water.

$$CH_3N(NO)CONH_2 + KOH \longrightarrow CH_2N_2 + KCNO + 2H_2O$$

3. Standard Methyl Benzoate - A standard solution of 126.5 micrograms per microliter methyl benzoate in ether was prepared.

The operating conditions used for the gas chromatograph are:

Perkin-Elmer Model 3980A gas chromatograph
Tenax-GC column (4-ft x 1/8-in stainless steel)
185°C column temperature
70 ml/min nitrogen carrier gas flow
50 ml/min hydrogen gas flow to detector
35 ml/min air flow to detector
200°C detector temperature
240°C injector temperature

A preliminary experiment was done to test the efficiency of this alternate method. Three vials containing 5 ml ether were spiked with 450 micrograms benzoyl peroxide. To this solution 1 ml KI reagent and 2 ml diazomethane reagent were added. The solutions were transferred to 10-ml volumetric flasks and brought to volume with ether. A standard for methyl benzoate was prepared by dissolving methyl benzoate in ether to give a concentration of 126.5 mg/ml of methyl benzoate in ether. Appropriate aliquots were drawn and dilutions were made in ether to prepare working standards in the range of 8 micrograms/ml to 130 micrograms/ml. A calibration curve was prepared and the amount of methyl benzoate in the samples was determined from this curve. No correction was necessary for the blank.

Table S253-10

mg benzoyl peroxide taken	equivalent mg methyl benzoate		mg methyl benzoate found
0.450	0.506		0.482
0.450	0.506		0.488
0.450	0.506		0.472
		mean	0.481
		% Recovery	95%

This value (0.95) was used to correct for the number of mg of benzoyl peroxide found when analysis was done by this method above.

After collection of the samples from test atmospheres, each filter was extracted with 10 ml of ether. Part of this solution was used for analysis by liquid chromatography. A 5-ml aliquot was placed in a 10-ml volumetric flask, the benzoyl peroxide reduced with iodide ion, and the resulting benzoic acid derivatized by addition of diazomethane. After bringing to volume, these samples were analyzed by gas chromatography.

All of the samples taken for validation were analyzed by liquid chromatography; only those listed in Table S253-11 were analyzed also by gas chromatography. In the remaining samples, the volume of solution used during liquid chromatographic analysis was greater than 5 ml, thereby leaving an insufficient volume for the alternate analysis.

The concentration of benzoyl peroxide found by each of these two methods was compared for each sample. The results are presented below in Table S253-11.

Table S253-11

Comparison of Results of Analysis by
Liquid Chromatography and Gas Chromatography

Filter No.	Concentration of Benzoyl Peroxide (mg/cu m) By Liquid Chromatography (A)	By Gas Chromatography (B)	Ratio (A:B)
1	3.03	2.90	1.04
2	3.16	2.97	1.06
3	3.28	2.97	1.10
4	2.97	3.22	0.92
5	3.16	3.04	1.04
6	7.08	7.58	0.93
7	7.13	8.13	0.88
8	7.17	8.60	0.83
9	7.39	7.91	0.93
10	18.48	17.46	1.06
11	19.29	17.32	1.11
12	18.90	16.76	1.13
		mean	1.00
		std dev	0.10
		CV	0.10

Although the average overall ratio of the concentration found by liquid chromatography to the concentration found by gas chromatography of the derivative is 1.00, it should be noted that the coefficient of variation for these 12 samples is 0.10. Further, the average ratios for the three concentration levels are 1.03, 0.89, and 1.10.

A satisfactory explanation for these differences was not evident. Any benzoic acid present in the generation system resulting from reduction of benzoyl peroxide during generation would be a positive interference in the gas chromatographic analysis, and the ratios found would all be less than 1.0, rather than have the ranges noted. It should be noted that the solution concentration levels of the derivatized product necessitated operating the gas chromatograph at a high sensitivity, and these analyses were more difficult to perform quantitatively. It is not believed that the results of this test are evidence that a bias exists in the sampling and analytical method. Therefore, no recovery correction should be applied to the concentration found. It was assumed that the method described in S253 is the best available and that the taken and found results are identical.

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 6. A summary is given in Attachment C.

The precision of the analytical method was assessed using the data in Table S253-12. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.024.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S253-13 and the results from the storage stability and collection efficiency tests. The pooled Coefficient of Variation (CV_2) for the three sets of samples collected from test atmospheres is 0.032.

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 0.060.

Table S253-12

Data Sheet: Benzoyl Peroxide

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.
0.225	0.201	0.893	0.450	0.438	0.973	0.900	0.839	0.932
0.225	0.211	0.938	0.450	0.449	0.998	0.900	0.855	0.950
0.225	0.215	0.956	0.450	0.448	0.996	0.900	0.860	0.956
0.225	0.220	0.978	0.450	0.446	0.991	0.900	0.862	0.958
0.225	0.218	0.969	0.450	0.440	0.978	0.900	0.894	0.993
0.225	0.220	0.978	0.450	0.439	0.976	0.900	0.862	0.958
n =		6			6			6
mean		0.952			0.985			0.958
std dev		0.033			0.011			0.020
CV_1		0.035			0.011			0.021

$\overline{CV}_1$ 0.024

$\overline{CV}_{A+\overline{AMR}}$ 0.026

Table S253-13

Data Sheet: Benzoyl Peroxide

Sampling and Analysis

Test Level	Found			
	mg	Corr. mg**	Liters	mg/cu m*
0.5X	0.288	0.298	98.4	3.03
	0.303	0.314	99.5	3.16
	0.309	0.320	97.4	3.28
	0.274	0.284	95.5	2.97
	0.282	0.292	92.4	3.16
	This sample was dropped, because it did not pass the Grubbs' outlier test at the 1% confidence level.			
			n = 5	
			mean	3.12
			std dev	0.12
			CV_2	0.038
1X	0.627	0.650	84.0	7.74
	0.628	0.651	92.0	7.08
	0.616	0.638	89.5	7.13
	0.592	0.613	85.5	7.17
	0.612	0.634	85.8	7.39
	This sample was dropped, because of a malfunctioning orifice.			
			n = 5	
			mean	7.30
			std dev	0.27
			CV_2	0.037
2X	1.609	1.667	90.2	18.48
	1.701	1.763	91.4	19.29
	1.649	1.709	90.4	18.90
	1.793	1.858	95.9	19.37
	1.790	1.855	95.0	19.53
	1.766	1.830	96.2	19.02
			n = 6	
			mean	19.10
			std dev	0.38
$\overline{CV_2}$ 0.032			CV_2	0.020

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 6.

**An analytical method recovery (A.M.R.) of 0.965 was used to calculate corr. mg.

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. Johnson, R. M. and Siddiqi, I. W., The Determination of Organic Peroxides, Pergamon, New York, (1970), 15-28.

3. Skellon, J. H. and Wills, E. D., Analyst, 73, (1948), 78.

4. Tabolsky and Mesrobian, Organic Peroxides, Interscience Publishers, Inc., New York, (1954).

5. Arndt, F., Org. Syntheses, Coll. Vol. 2, (1943), 166.

6. 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 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.

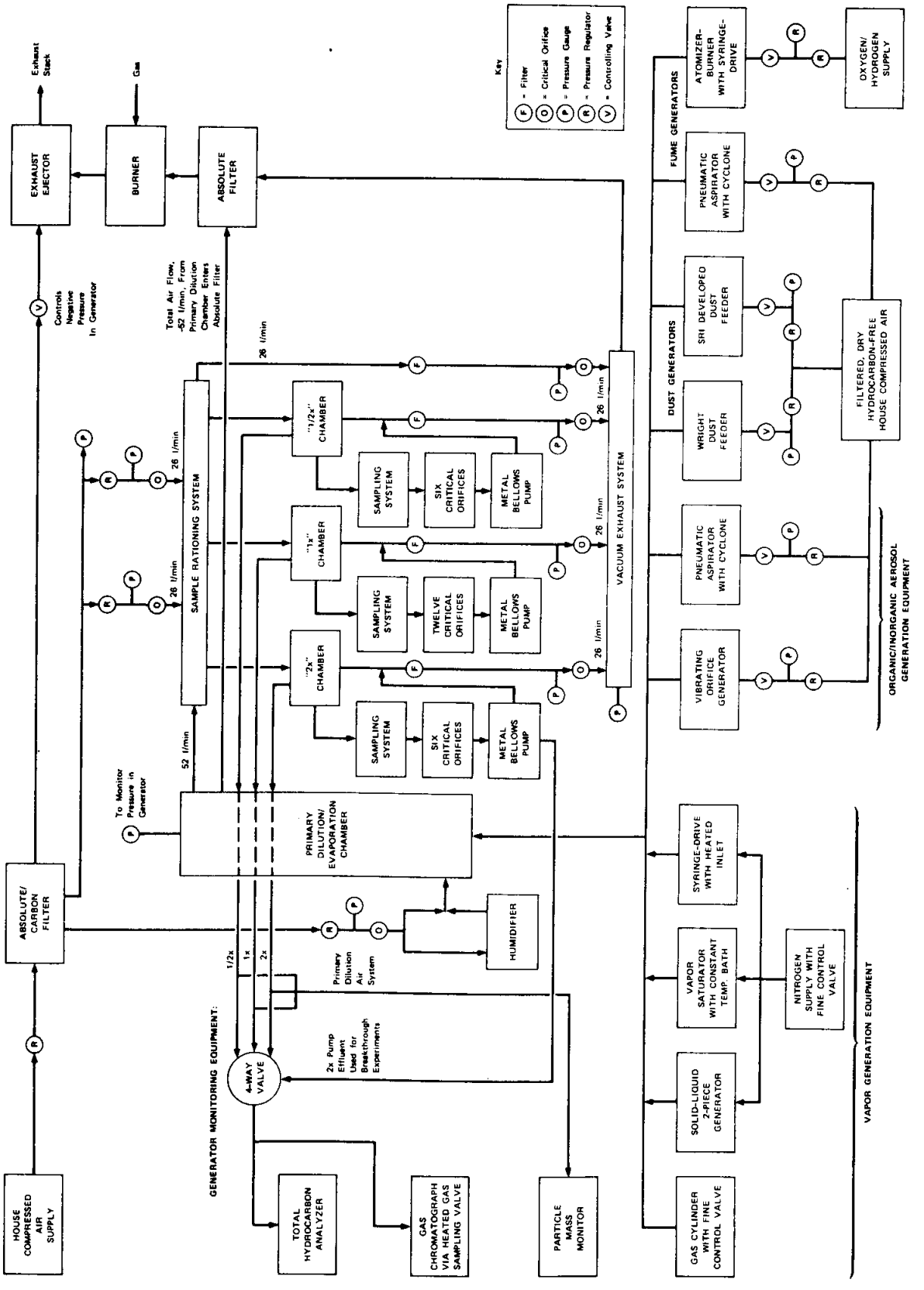


FIGURE S253-1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

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.

Chlorodiphenyl, 42% chlorine

Analyte:	Chlorodiphenyl, 42% chlorine	Method No.:	S120
Matrix:	Air	Range:	0.51-2.7 mg/cu m
OSHA Standard:	1 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.092
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date:	12/24/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series with a midget bubbler containing 15 ml of iso-octane to collect chlorodiphenyl, 42% chlorine.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial, and an aliquot of the sample is analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.507-2.747 mg/cu m at an atmospheric temperature of 23.5°C and atmospheric pressure of 766 mm Hg, using a 235-liter sample.

2.2 The upper limit of the range of the method is dependent on the capacity of the glass fiber filter connected in series to the midget bubbler and the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

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. This is particularly important, because chlorodiphenyl, 42% chlorine, is a mixture.

3.2 Chlorodiphenyl, 42% chlorine, gives a characteristic envelope shaped gas chromatographic curve for a number of unresolved peaks. Any other compound that has the same retention time as chlorodiphenyl, 42% chlorine, at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.507-2.747 mg/cu m was 0.092. 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 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method. 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 evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

5.3 Another 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.

5.4 Chlorodiphenyl, 42% chlorine, is a mixture of isomers. Under the gas chromatographic conditions used for validation an "envelope" of peaks was analyzed. The quantitation of area is difficult unless an integrator is used. It is likely that samples may give slightly different shaped envelopes than standards.

5.5 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.

5.6 Scintillation vials are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the vials during shipping.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter glass fiber filter (Gelman Type AE or equivalent) and a polystyrene 37-mm two-piece cassette filter holder. The filter is held in the two-piece filter holder, supported by a stainless steel support screen. The filter must be free of organic binders. Filter holders made of Tenite should not be used. Secure the cassette holder together with tape or a shrinkable band.

6.2 A glass midget bubbler containing 15 ml of iso-octane.

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 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.4 Manometer.

6.5 Thermometer.

6.6 Scintillation vials: 20 ml, with Teflon cap liners (22-mm) for proper seal. Add 15 ml of distilled water into each vial and mark the liquid level. Pour out the water and dry each vial.

6.7 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor Coulson Conductivity Detector or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge. The gas chromatograph must be equipped with a temperature programmer.

6.8 Column (1.5 m x 2-mm I.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.9 An electronic integrator or some other suitable method for measuring areas of the envelope of unresolved peaks.

6.10 Microliter syringes: 25-microliter for making GC injections.

6.11 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.12 Pipets: 15-ml pipets for measuring the collection medium, and other convenient sizes for preparing standard solutions.

7. Reagents

7.1 Chlorodiphenyl, 42% chlorine.

7.2 Iso-octane, nanograde.

7.3 Nitrogen, purified.

7.4 Hydrogen, prepurified.

8. Procedure

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

8.2 Calibration of Personal Sampling Pump. Each personal sampling pump

must be calibrated with a representative filter cassette and bubbler 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 two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of iso-octane into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked at least every 15 minutes. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the solution at the end of sampling should be 12 ml or less.

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 arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. 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 270 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.

8.3.8 After sampling remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.

8.3.9 Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding the rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

8.3.10 The glass fiber filter should be removed from the cassette filter holder and placed in the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vials with appropriate caps with Teflon liners.

8.3.11 Carefully record the sample identity, all relevant sampling data, and the type of sampling pump used.

8.3.12 With each batch of ten samples submit one filter and bubbler 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.

8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit. These samples must not be sent through the mail. The Department of Transportation Regulations do not permit the shipment of these samples in containers that will prevent breakage and leakage of these samples.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Before injection of the sample into the GC, swirl the contents in the vials to ensure thorough mixing.

8.4.2 Appropriate blanks must be analyzed at the same time as the samples.

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

220°C inlet temperature
column temperature program from 120°C-220°C as described below.
150 ml/min nitrogen carrier gas flow
150 ml/min hydrogen gas flow to detector furnace
820°C detector furnace temperature
250°C transfer temperature
250°C vent temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, a solvent flush injection technique should be used. The 25-µl 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 1.0 microliter to separate the sol-

vent 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 15-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 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The sample is injected slowly over a time period of 10 seconds. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 30 seconds was adequate to elute the solvent. After 30 seconds, close the vent and begin temperature programming at a rate of 7.5°C per minute. The initial temperature should be 120°C and the final temperature should be 220°C. The final temperature is held for 5 minutes. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area. The area of the envelope 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.

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 size 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 mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

9.1 Prepare a stock standard solution by weighing 1 gram of the analyte and add to a 100-ml volumetric flask. Make to volume with acetone and mix thoroughly. Acetone is preferred as a solvent for the stock standard solution, because the analyte dissolves readily in acetone at this concentration.

9.2 From the 10 microgram/microliter stock standard, appropriate aliquots are used to prepare at least five working standards to cover the range of 0.030-0.810 mg/15 ml. This range is based on a 270-liter air sample. Prepare all working standards in iso-octane.

9.3 Prepare a standard calibration curve by plotting concentration in mg/15 ml versus areas of peak envelopes.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane, 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.

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

where:

mg sample = mg found in sample filter and bubbler

mg blank = mg found in blank filter and bubbler

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 chlorodiphenyl, 42% chlorine, in the air sample can be expressed in mg/cu m.

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

11. References

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

11.2 Backup Data Report for Chlorodiphenyl, 42% chlorine, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S120

Substance

Chlorodiphenyl, 42% chlorine

Standard

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

Analytical Method

A known volume of air is drawn through a glass fiber filter connected in series with a midget bubbler containing 15 ml of iso-octane to trap the chlorodiphenyl, 42% chlorine, present. The solution in the midget bubbler is transferred to a 20-ml scintillation vial and the filter is added. The analyte is separated and analyzed using a gas chromatograph with an electrolytic conductivity detector. The method has been validated over the range of 0.507-2.747 mg/cu m for a 235-liter sample at 23.5°C and 766 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 diameter glass fiber filter connected in series with a midget bubbler. The filter must be free of organic binders. The filter holder should be made of polystyrene. Do not use filter holders made of Tenite. The filter is held in the filter holder supported by a stainless steel support screen. The sampling pump is protected from splash-over or solvent condensation by a 5-cm long x 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump. (One hundred milliliters of iso-octane should accompany each set of samples for rinsing the bubbler stems and transferring the contents of the bubblers to the scintillation vials.) The scintillation vials which are used for shipping should be marked at 15 ml.

Sample Size

A sample size of 270 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. Pipet 15 ml of the collection medium (iso-octane)

into each bubbler and mark the liquid level. The liquid level in the bubbler must be checked at least every 15 minutes. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximatley 15 minutes before the end of sampling. The final volume at the end of sampling should be 12 ml or less.

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 arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. 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, remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.

6. Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

7. Remove the glass fiber filter from the cassette filter holder and place into the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vial with an appropriate cap with a Teflon cap liner.

8. Carefully record the sample identity and all relevant sampling data.

9. With each batch of ten samples submit one filter and midget bubbler 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 scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit. These samples must not be sent through the mail. The Department of Transportation Regulations do not permit the shipment of these samples in containers that will prevent breakage and leakage of these samples.

Reference

Chlorodiphenyl, 42% chlorine, NIOSH Method No. S120.

Backup Data Report

Substance:	Chlorodiphenyl, 42% chlorine , No. S120
OSHA Standard:	1 mg/cu m - skin
Chemical Used for Validation:	Arochlor 1242, Lot KD 12-418 Monsanto

General

The procedure for collection and analysis of air samples of chlorodiphenyl, 42% chlorine, is described in NIOSH Method No. S120. This method consists of collecting the sample on a glass fiber filter connected in series with a midget bubbler containing iso-octane, and analyzing the resulting sample by gas chromatography.

This method has been tested for validity for a 235-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 chlorodiphenyl, 42% chlorine, to represent 270-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 collection efficiency of the glass fiber filters connected in series to midget bubblers.

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. S120. The results of the analytical method recovery tests are in Table S120-1.

The appropriate aliquot (2, 4, and 8 microliters) of a 67.5 mg/ml solution of chlorodiphenyl, 42% chlorine, in acetone was added to 37-mm Type AE glass fiber filters. Chlordiphenyl, 42% chlorine, was extracted with iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector. The gas chromatograph was temperature programmed, and the area of an envelope of peaks was measured.

Sampling and Analysis

Samples of chlorodiphenyl, 42% chlorine, in air were generated by the procedure described in Attachments A and B and collected as described in Method No. S120.

A 5 g/liter solution of chlorodiphenyl, 42% chlorine, in a 50/50 mixture of methanol and acetone was used in the aspiration system for the generation of the analyte. To obtain the desired concentration, a set of generation conditions was chosen, and 30-minute samples 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 at each of 2X, 1X, and 0.5X the OSHA standard level.

The samples were collected for 180 minutes at flow rates of approximately 1.4 liter/minute. The results of the analysis of the 18 generated samples are presented in Table S120-2.

Collection Efficiency

Collection efficiency tests were conducted at 2.747 mg/cu m (as determined by analysis of samples collected at 2X the OSHA standard level) by mounting in series one filter to two midget bubblers, each containing 15 ml of iso-octane. The results of the collection efficiency test are given below:

Table S120-3

	mg/cu m found in filter and first backup bubbler	mg/cu m found in second backup bubbler	Collection Efficiency
	2.880	N.D.*	1.00
	2.665	N.D.*	1.00
	2.558	N.D.*	1.00
	2.896	N.D.*	1.00
	2.690	N.D.*	1.00
	2.793	N.D.*	1.00
mean	2.747		
std dev	0.132		
CV	0.048		

*N.D. = Not detected at a detection limit of 0.014 mg/cu m.

From the above results, it has been demonstrated that chlorodiphenyl, 42% chlorine is collected efficiently on a glass fiber filter connected in series with a single midget bubbler containing 15 ml of iso-octane. Since collection efficiency was determined to be 1.00, no correction for

collection is needed.

Storage Stability

A storage stability test was conducted to assess whether chlorodiphenyl, 42% chlorine, would be successfully stored for one week after collection. Six samples were collected at 1X the OSHA standard level. An aliquot of each sample was analyzed immediately, and the remainder of the samples were stored for one week before analysis. The results are presented below:

Table S120-4

	Analyzed Immediately mg/cu m	Analyzed After 7 Days mg/cu m
	1.132	1.163
	1.169	1.169
	1.207	1.209
	1.194	1.191
	1.217	1.258
	1.159	1.143
mean	1.180	1.189
std dev	0.032	0.041

$$\text{Recovery} = \frac{7 \text{ days}}{\text{Immediate}} = 1.008$$

The above results indicate that chlorodiphenyl, 42% chlorine, is stable in iso-octane for at least one week.

Independent Method

A concerted but unsuccessful effort was made to use fluorescein as a tracer dye to determine the concentration in the sample generator. Known amounts of fluorescein and chlorodiphenyl, 42% chlorine, in a 50/50 mixture of methanol and acetone were used in the aspiration system. Extra samples were collected on filters and analyzed for fluorescein. The fluorescein content of these filter samples was compared with the chlorodiphenyl, 42% chlorine, content of the corresponding samples collected with the filter-bubbler combination. The chlorodiphenyl, 42% chlorine, content of the samples was higher than predicted by comparison with the fluorescein level. The causes for this discrepancy are not known. There was apparently a selective loss of fluorescein in the sample generator. The method showed enough promise to warrant further development of the dye tracer method for use in future studies on other materials. However, it was abandoned in the present study due to the lack of time.

Three samples were collected at 2X the OSHA standard level using 37-mm glass fiber filters connected in series with midget bubblers containing toluene (15 ml) instead of iso-octane. Iso-octane was used as the collection medium for the samples used for validation of the sampling and analytical method. These samples were found to contain 2.85, 2.90, and 2.94 mg/cu m in agreement with those collected on filters backed up with bubblers containing iso-octane.

Although considerable effort was expended to develop an independent method of verifying the concentration of chlorodiphenyl, 42% chlorine, in the generator without success, it was necessary to use the implicit method based on eliminating all of the known possible biases in the method. It was therefore assumed that the method described in S120 is the best available method and that the taken and found results are identical.

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2. A summary is given in Attachment C.

The precision of the analytical method was assessed using the data in Table S120-1. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.067.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S120-2 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 0.072.

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 0.092.

Table S120-1

Data Sheet: Chlorodiphenyl, 42% chlorine

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.
0.1347	0.1377	1.022	0.2694	0.2808	1.042	0.539	0.610	1.132
0.1347	0.1464	1.087	0.2694	0.2891	1.073	0.539	0.514	0.954
0.1347	0.1457	1.082	0.2694	0.2532	0.940	0.539	0.506	0.939
0.1347	0.1347	1.000	0.2694	0.2345	0.870	0.539	0.496	0.920
0.1347	0.1354	1.005	0.2694	0.2594	0.963	0.539	0.546	1.013
0.1347	0.1317	0.978	0.2694	0.2737	1.016	0.539	0.553	1.026
	n =	6			6			6
	mean	1.029			0.984			0.997
	std dev	0.045			0.074			0.078
	CV_1	0.044			0.075			0.078

$$\overline{CV}_1 \cdot 0.067$$

$$\overline{CV}_{A+\overline{AMR}} \; 0.072$$

From the above results, no Analytical Method Recovery (A.M.R.) correction is necessary.

Table S120-2

Data Sheet: Chlorodiphenyl, 42% chlorine

Sampling and Analysis

Test Level	Found		
	mg	Liters	mg/cu m**
0.5X	0.1404	245.5	0.572
	0.0670	124.6	0.538
	0.1201	240.6	0.499
	0.1174	240.6	0.488
	0.0987	242.2	0.408
	0.1304	242.2	0.538
		n = 6	
		mean	0.507
		std dev	0.057
		CV_2	0.112
1X	0.2845	251.3	1.132
	0.2870	245.5	1.169
	0.2982	247.1	1.207
	0.2923	244.8	1.194
	0.3021	248.2	1.217
	0.2843	245.3	1.159
		n = 6	
		mean	1.180
		std dev	0.032
		CV_2	0.027
2X	0.665	230.9	2.880
	0.623	233.8	2.665
	0.593	231.8	2.558
	0.675	233.1	2.896
	0.624	232.0	2.690
	0.644	230.6	2.793
		n = 6	
		mean	2.747
		std dev	0.132
$\overline{CV_2}$ 0.072		CV_2	0.048

**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, NIOSH Contract CDC-99-74-45.

Attachment A

Generation of Organic Particulates

Test atmospheres of organic particulates can be generated by an aspiration/spray-dry technique. The aerosol generation system (Figure A1) consists of a fluid aspirator, an impactor and two cyclones which remove droplets greater than two microns in diameter, and mixing chamber where solvent evaporates from the aerosol droplets. The aspirator, impactor, and primary cyclone are made of Pyrex glass. The secondary cyclone is constructed of Teflon. The mixing chamber is stainless steel.

The aspiration unit (Figure A2) consists of a 0.5-mm capillary tube and a concentric outer tube. The tip of the 0.5-mm capillary tube is ground until the wall thickness at the exit of the tube is no more than 0.25 mm. The end of the outer tube is tapered so that the clearance between the tip of the capillary tube and the concentric outer tube is about 0.5 mm. The aspirator air at several psig passes through the outside tube at a high velocity. Liquid is drawn up the capillary tube and is aspirated at the tip where an aerosol is formed. The aerosol impacts on the roof of the primary separation chamber, where the largest droplets are removed. The remaining aerosol then passes into the primary cyclone which passes droplets less than about six microns in diameter. The secondary cyclone passes droplets less than two microns in diameter. The large droplets which are impacted against the walls of the primary separation chamber and the primary cyclone, eventually re-enter the liquid supply, thereby recycling the unused solution. Droplets collected from the secondary cyclone fall into a small attached flask.

Recycling the impacted aerosol minimizes the increase in the solution concentration due to vaporization of the solvent. Increased solution concentration would cause the aerosol particle size to increase as a function of time, which in turn would lead to an increase in the concentration of the aerosol particles.

Aerosol droplets enter the mixing chamber and mix with high velocity dilution air. Turbulent mixing of the dilution air and the aerosol takes place. The residence time in the mixing chamber is sufficient for solvent evaporation from the droplets to occur.

Generation of aerosols at the desired concentration is accomplished by adjusting the flows of air through the aspirator and of the primary dilution air.

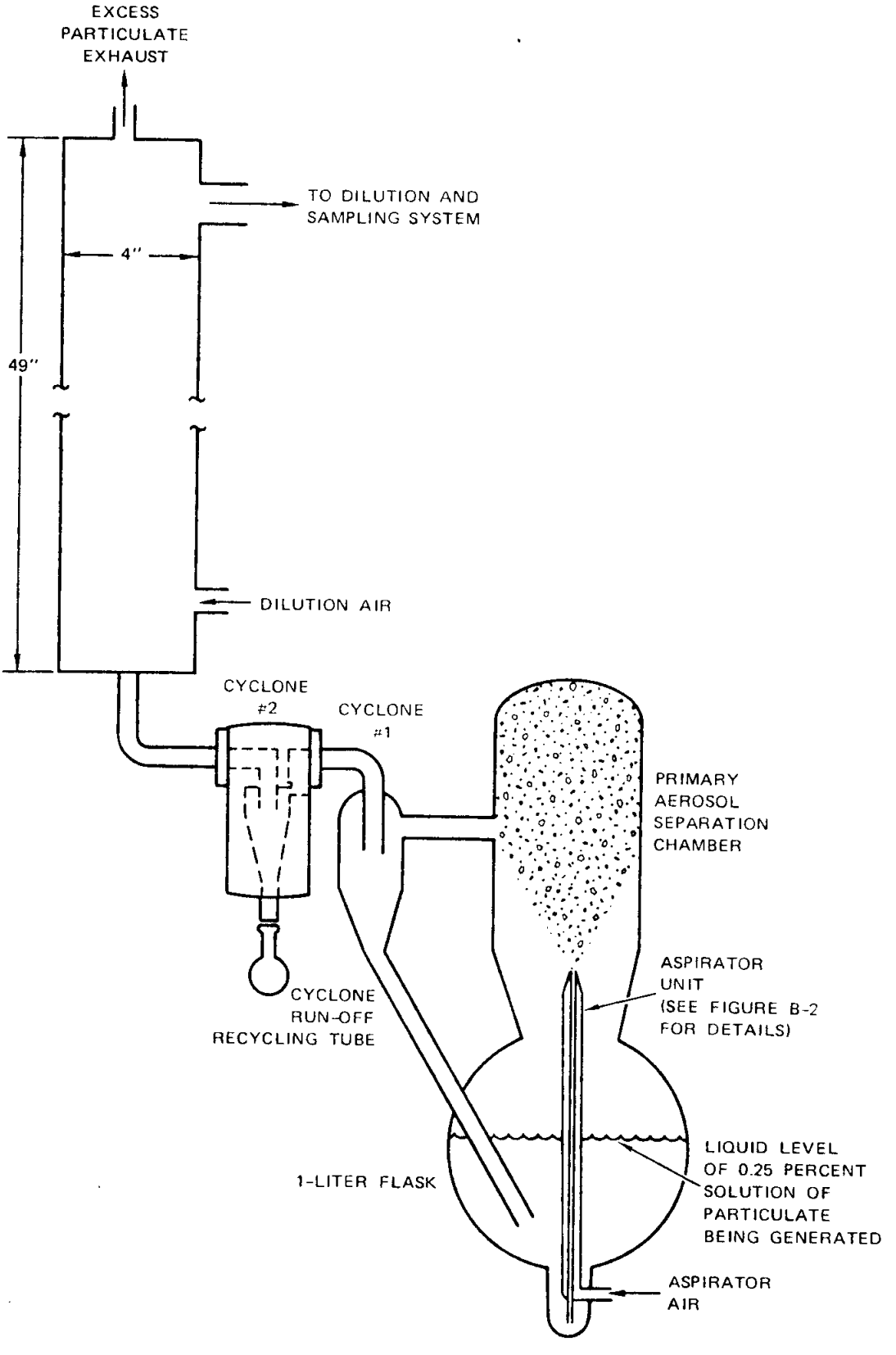


FIGURE S120-A1 PARTICLE GENERATOR

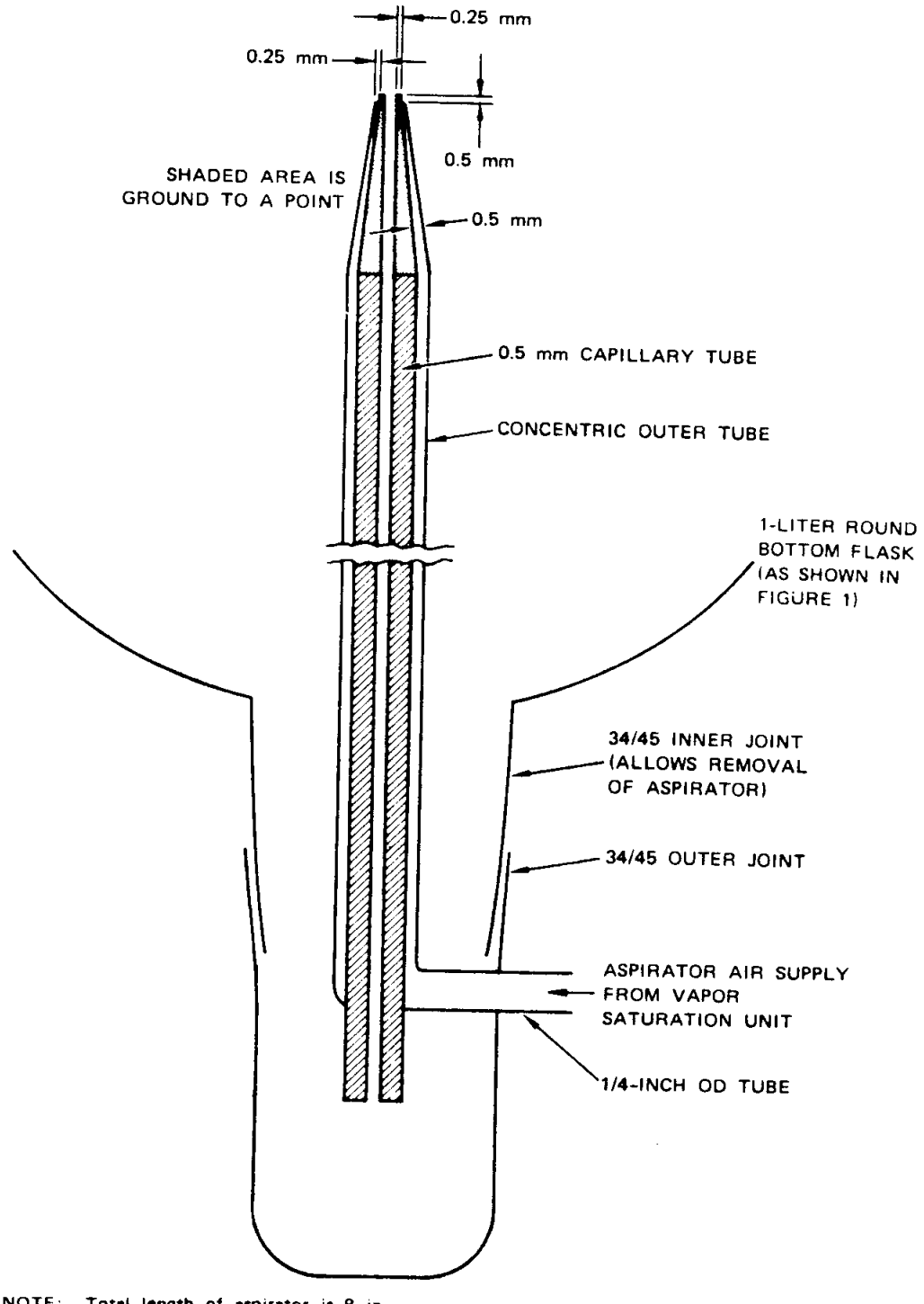


FIGURE S120-A2 ASPIRATOR DETAILS

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 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

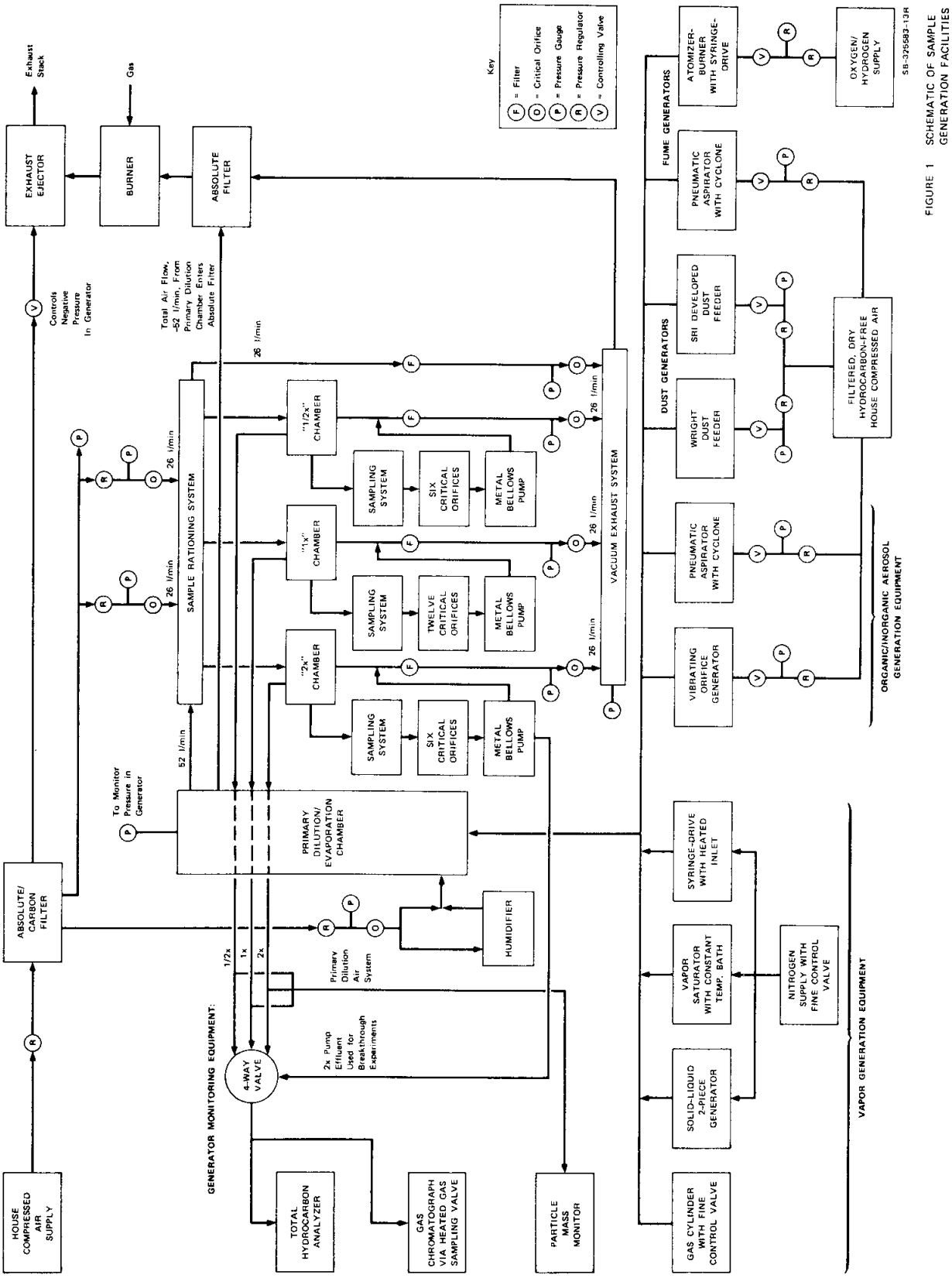


FIGURE 1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

(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

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.

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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.

$$\overline{CV}_S = \sqrt{(\overline{CV}_2)^2 - (\overline{CV}_1)^1}$$

$\overline{CV}_P$ - 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.

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Furfuryl Alcohol

Analyte:	Furfuryl Alcohol	Method No.:	S365
Matrix:	Air	Range:	120-470 mg/cu m
OSHA Standard:	50 ppm (200 mg/cu m)	Precision ($\overline{CV}_T$):	0.072
Procedure:	Adsorption on Porapak Q, desorption with acetone, GC	Validation Date:	2/18/77

1. Principle of the Method

1.1 A known volume of air is drawn through a glass tube containing Porapak Q to trap furfuryl alcohol vapors.

1.2 Furfuryl alcohol is desorbed from the Porapak Q with acetone, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 117-469 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 765 mm Hg, using a 6-liter sample. This sample size is based on the capacity of the Porapak Q to collect vapors of furfuryl alcohol 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 Porapak Q. This capacity may vary with the concentrations of furfuryl alcohol and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for seven hours at an average sampling rate of 0.044 liter/minute and relative humidity of greater than 80% and temperature of 19°C. The breakthrough test was conducted at a concentration of 418 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 furfuryl alcohol 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 117-469 mg/cu m was 0.072. This value corresponds to a 34 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 1.6% 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 224.2 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 furfuryl alcohol found on the backup section of the Porapak Q 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 Porapak Q Tubes: Glass tube with both ends unsealed, 8.5-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 50/80 mesh Porapak Q* separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Porapak Q, and the backup section contains 75 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 0.05 liter per minute. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. The Porapak Q tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to useage, Porapak Q 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 Porapak Q is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Porapak Q 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 (3-ft long x 1/8-inch O.D. stainless steel)packed with 50/80 mesh Porapak Q.

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 Polyseal** caps or equivalent.

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.

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* Porapak Q is a solid adsorbent which is manufactured by Waters Associates, Inc., and is commonly used as a gas chromatographic column packing material.

** The Polyseal Corp., Baltimore, Maryland.

6.11 Manometer.

7. Reagents

7.1 Acetone, reagent grade.

7.2 Furfuryl alcohol, "Baker Grade" from J. T. Baker Chemical Company or equivalent. Furfuryl alcohol is a clear viscous liquid. If furfuryl alcohol is received from the manufacturer as a dark colored liquid, it should be distilled before use. The boiling point of furfuryl alcohol is 170°C.

7.3 Benzene, chromatographic quality.

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, 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 Porapak Q tube in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.3)

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of Porapak Q 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 Porapak Q.

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

8.3.5 A sample size of 6 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. Do not sample at a flow rate less than 0.010 liter per 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 Porapak Q 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 Porapak Q 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 Polyseal cap. This sample should not be transported in the same container as the Porapak Q tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Porapak Q tube. Remove the glass wool plug and transfer the first (larger) section of Porapak Q to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Porapak Q to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to affect complete transfer of the Porapak Q.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the furfuryl alcohol 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
65 ml/min (24 psig) hydrogen gas flow to detector
500 ml/min (50 psig) air flow to detector
225°C injector manifold temperature
225°C detector manifold temperature
200°C column temperature

A retention time of approximately 11 minutes is to be expected for furfuryl alcohol under these conditions and using the

column recommended in Section 6.4. The acetone will elute from the column before the furfuryl alcohol.

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 Porapak Q.

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 Porapak Q 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 Porapak Q.

8.5.2 Porapak Q equivalent to the amount in the first section of the sampling tube (150 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This Porapak Q must be from the same batch as that used in obtaining the samples. The open end is capped with Parafilm. A known amount of a benzene solution of furfuryl alcohol containing 300 mg/ml is injected directly into the Porapak Q with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 6-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the Porapak Q, because the amounts to be added would be too small to measure accurately.

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 assure complete adsorption of the furfuryl alcohol onto the Porapak Q. 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 furfuryl alcohol into 1.0 ml of acetone 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 mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of furfuryl alcohol collected on the Porapak Q. Plot the desorption efficiency versus weight of furfuryl alcohol 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 mg/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 a stock standard solution containing 120 mg/ml of furfuryl alcohol in acetone.

9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in acetone. Prepare at least 5 working standards to cover the range of 0.12-3.6 mg/1.0 ml. This range is based on a 6-liter sample.

9.3 Prepare a standard calibration curve by plotting concentration of furfuryl alcohol in mg/1.0 ml versus peak area.

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/1.0 ml acetone 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.

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg 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 mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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 furfuryl alcohol in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 furfuryl alcohol
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

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

11.2 Backup Data Report for Furfuryl Alcohol, 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. S365

Substance

Furfuryl Alcohol

Standard

8-hour time-weighted average: 50 ppm (200 mg/cu m)

Analytical Method

A known volume of air is drawn through a tube containing 50/80 mesh Porapak Q to trap the furfuryl alcohol vapors present. The furfuryl alcohol is desorbed from the Porapak Q with acetone 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 117-469 mg/cu m for a 6-liter sample at 22°C and 765 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 0.05 liter per minute. A tube (8.5 cm long with a 6-mm O.D. and a 4-mm I.D.), containing two sections of 50/80 mesh Porapak Q separated by a 2-mm portion of urethane foam, is used to collect the samples. The front section of the tube contains 150 mg of Porapak Q, and the back section contains 75 mg. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. Prior to packing, the Porapak Q is prewashed in acetone.

Sample Size

A sample size of 6 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. Do not sample at a flow rate less than 0.01 liter per minute.

Sampling Procedure

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

2. The smaller section of Porapak Q 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 Porapak Q tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of furfuryl alcohol.

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3. Air being sampled should not be passed through any hose or tubing before entering the Porapak Q 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 Porapak Q 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. With each batch of ten samples, submit one Porapak Q 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. Label this tube as a blank. Information on the batch number of the Porapak Q must be supplied. A minimum of 18 extra Porapak Q tubes should be provided for desorption efficiency determinations.

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 Porapak Q 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 Polyseal* cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Capped Porapak Q 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

Furfuryl Alcohol, NIOSH Method No. S365

*The Polyseal Corp., Baltimore, Md.

Backup Data Report No. S365

Substance:	Furfuryl Alcohol
OSHA Standard	50 ppm (200 mg/cu m)
Chemical Used for Validation:	Furfuryl Alcohol from J. T. Baker Chemical Company The furfuryl alcohol received was labelled "Baker Grade" and was redistilled before use in the validation study. (B.P. 170°C)

General

The procedure for collection and analysis of air samples of furfuryl alcohol is described in NIOSH Method No. S365. This method consists of collection of the sample on Porapak Q, desorption with acetone, and analysis of the resulting solution by gas chromatography.

This method has been tested for validity for a 6-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 furfuryl alcohol to represent 6-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 Porapak Q 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. S365. The results of the desorption efficiency tests are in Table S365-2. Porapak Q, Lot 1271, was used in the validation study.

Sampling and Analysis

Test atmospheres of furfuryl alcohol in air were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with a 50/50 mixture of furfuryl alcohol in water and placed in the syringe drive pump. A 15-inch long stainless steel needle was attached to the syringe. The needle passed through a rubber septum which enters into a heated glass tube. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen. It was diluted with air immediately downstream from the heated zone to obtain 2X the OSHA standard level. The dilution air was preheated prior to mixing with the furfuryl alcohol from the generator. The dilution air entered a copper coil (5 feet long) which was heated in an oil bath at 45°C. Heating the dilution air was necessary to avoid condensation of the furfuryl alcohol in the generation system. Dilutions to 1X and 0.5X the OSHA standard level were made as described in Attachment A. A total hydrocarbon analyzer, which was calibrated with bag standards, was used to monitor the stability of the concentration of furfuryl alcohol in each of the three test chambers and was also used as an independent measure of the generator concentration. The samples were collected as described in Method S365 using sampling tubes packed with 50/80 mesh Porapak Q.

Six samples were collected from each chamber for 135.5 minutes to obtain 6-liter air samples. An additional six samples were collected at 1X the OSHA standard level and were used for storage stability tests. The results of the analyses of the samples used for the validation study are in Table S365-3. 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 20 mg/cu m.

Storage Stability Study

A study was done to assess whether furfuryl alcohol 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. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results of the analyses are given below:

Table S365-1

	Samples Analyzed Immediately (mg/cu m)	Samples Analyzed After 7 Days (mg/cu m)
	185.4	194.4
	209.2	206.6
	214.0	209.1
	207.3	204.6
	208.8	196.5
	215.4	188.9
mean	206.7	200.0
std dev	10.9	7.9
CV	0.053	0.040

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 3%; thus, the storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed with the relative humidity greater than 80%. Details of the method of generating atmosphere containing high relative humidities are given in Attachment B. The test atmosphere was generated using the apparatus described in Attachment C. The generation parameters used during the breakthrough test are as follows:

Oil bath: 33°C
Nitrogen flow rate: 1.60 liter/minute at 19°C
Dilution air flow rate: 27.4 liters/minute

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) 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 sample, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

The breakthrough time was measured by testing in parallel six sampling tubes, each containing 150 mg of Porapak Q. The tubes were placed in the sample generation apparatus. The test atmosphere was caused to flow through each tube at the flow rates to be used during sample collection. Sampling flow rates were regulated with the use of 0.003-inch orifices for a rate of 0.044 liter per minute. The orifices were connected to a manifold, which was evacuated to about 22 inches of Hg using a metal bellows pump. This pump was selected, because it does not leak and is constructed entirely of stainless steel; therefore, it will not alter the composition of the test atmosphere.

A total hydrocarbon analyzer, which was calibrated with bag standards, was used to monitor the concentration of the generator during the breakthrough test.

Breakthrough did not occur when the average sampling rate was 0.044 liter per minute when the relative humidity was greater than 80%. The concentration tested was 418 mg/cu m. Sampling was discontinued after seven hours. Based on this information, the sample size should not exceed 12 liters. It was decided that a 6-liter sample would give an adequately long sampling time and sufficient sensitivity in the analytical method.

Independent Method

The concentration of furfuryl alcohol in each of the three stages of the generator was monitored during generation of the 0.5X, 1X, and 2X levels

with a total hydrocarbon analyzer which was calibrated with bag standards. The 2X bag standards were prepared by combining 4 microliters of furfuryl alcohol with air at a flow rate of 0.958 liter/minute for 709 seconds at 22°C and 765 mm Hg in a Tedlar plastic bag to give a concentration of 389.6 mg/cu m. The 1X bag standards were prepared by combining 2 microliters of furfuryl alcohol with air at a flow rate of 0.958 liter/minute for 709 seconds in a Tedlar plastic bag. The 1X bag standards were used to monitor the 1X and 0.5X sampling chambers, and the 2X bag standards were used to monitor the 2X sampling chamber. The data are summarized in Table S365-4.

Discussion

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. A GC analysis of an acetone extract of Porapak Q, Lot 1666, showed that a large amount of impurity was present. This impurity eluted soon after furfuryl alcohol. The impurity was not found on the Lot 1271 Porapak Q used in the validation study. In order to verify that this impurity did not adversely affect the method recoveries of furfuryl alcohol, the following study was done.

Two samples were prepared at 1X the OSHA standard level by spiking 4 microliters of a stock solution of furfuryl alcohol in benzene containing 295 mg/ml onto 150 mg of Lot 1666 Porapak Q. The samples were desorbed with 1 ml of acetone and analyzed by gas chromatography. The results are presented below:

mg taken	mg found	D.E.
1.180	1.123	0.952
1.180	1.132	0.959
	mean	0.955

The above results were compared with the 1X desorption efficiencies in Table S365-2, which are the desorption efficiencies on Porapak Q, Lot 1271. The two desorption efficiencies compare within 4%.

A storage stability study was also conducted on the Lot 1666 Porapak Q. The samples were prepared as described above and allowed to stand on the laboratory bench for one week before analysis. The samples were desorbed with 1 ml of acetone and analyzed by gas chromatography. The results of the storage stability study are presented below:

mg taken	mg found	Recovery
1.180	1.080	0.915
1.180	1.099	0.931
1.180	1.120	0.949
	mean	0.932

The above recovery compare within 2% with the 1X desorption efficiency found on the Lot 1666 Porapak Q. It was concluded that furfuryl alcohol is stable on Porapak Q Lot 1666 for at least one week. This is in good agreement with data for Porapak Q Lot 1271 which was used in the storage stability tests summarized on page S365-2.

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2. A summary is given in Attachment D.

The precision of the analytical method was assessed using the data in Table S365-2. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.031.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S365-3 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 0.050. 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 98.4%. 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 0.072.

Table S365-2

Data Sheet: Furfuryl Alcohol

Analysis

Level	0.5X			1X			2X	
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
0.590	0.547	0.927	1.180	1.142	0.968	2.360	2.417	1.024
0.590	0.526	0.892	1.180	1.141	0.967	2.360	2.183	0.925
0.590	0.551	0.934	1.180	1.200	1.017	2.360	2.190	0.928
0.590	0.558	0.946	1.180	1.179	0.999	2.360	2.207	0.935
0.590	0.541	0.917	1.180	1.203	1.020	2.360	2.182	0.925
0.590	0.538	0.912	1.180	1.210	1.025	2.360	2.248	0.953
n =		6			6			6
mean		0.921			0.999			0.948
std dev		0.019			0.026			0.039
CV_1		0.021			0.026			0.041

$\overline{CV}_1$ 0.031

$\overline{CV}_{A+\overline{DE}}$ 0.033

The equation D.E. = $0.974 - e^{-5.45 \times \text{mg found}}$ was used to calculate the corr. mg in Table S365-3. A program for the use of this equation is given in Reference 3.

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Table S365-3

Data Sheet: Furfuryl Alcohol

Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr. mg	Liters	mg/cu m*	mg/cu m	Recovery (%)
0.5X	0.717	0.752	6.19	121.5	116.8	
	0.611	0.651	6.15	105.8	116.8	
	0.738	0.772	6.07	127.2	116.8	
	0.685	0.721	6.12	117.8	116.8	
	0.669	0.706	6.10	115.7	116.8	
	0.695	0.731	6.07	120.4	116.8	
			n = 6			
			mean	118.1		101.1
			std dev	7.2		
			CV_2	0.061		
1X	1.098	1.131	6.10	185.4	224.2	
	1.258	1.293	6.18	209.2	224.2	
	1.280	1.316	6.15	214.0	224.2	
	1.073	1.105	5.33	207.3	224.2	
	1.247	1.282	6.14	208.8	224.2	
	1.281	1.316	6.11	215.4	224.2	
			n = 6			
			mean	206.7		92.2
			std dev	10.9		
			CV_2	0.053		
2X	2.584	2.653	5.79	458	469	
	2.965	3.044	6.22	489	469	
	2.897	2.974	6.23	477	469	
	2.707	2.779	5.64	493	469	
	2.456	2.522	5.47	461	469	
	2.937	3.015	6.15	490	469	
			n = 6			
			mean	478		101.9
			std dev	15		
$\overline{CV}_2$ 0.050			CV_2	0.031		

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

Table S365-4

Sample Generator Data: Furfuryl Alcohol

Hydrocarbon Analyzer Chart Readings

	2X Bags	1X Bags	(Calculated from 2X Bags) 2X Chamber	(Calculated from 1X Bags) 1X Chamber	0.5X Chamber
	78.0	43.9	93.7	49.9	26.0
	79.5	43.5	93.8	50.1	26.4
	78.2		92.2	50.1	26.2
	79.0		95.6	51.0	26.4
	77.2		95.8		
			95.5		
			94.0		
			94.9		
mean	78.4	43.7	94.4	50.3	26.2
std dev	0.9	0.3	1.2	0.5	0.2
CV	0.011	0.007	0.013	0.010	0.008
mg/cu m	390	194.8	469	224.2	116.8

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, NIOSH Contract CDC-99-74-45.

3. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, ed., p. 387, (University of California Press, Los Angeles, California, 1973).

Attachment A

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 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

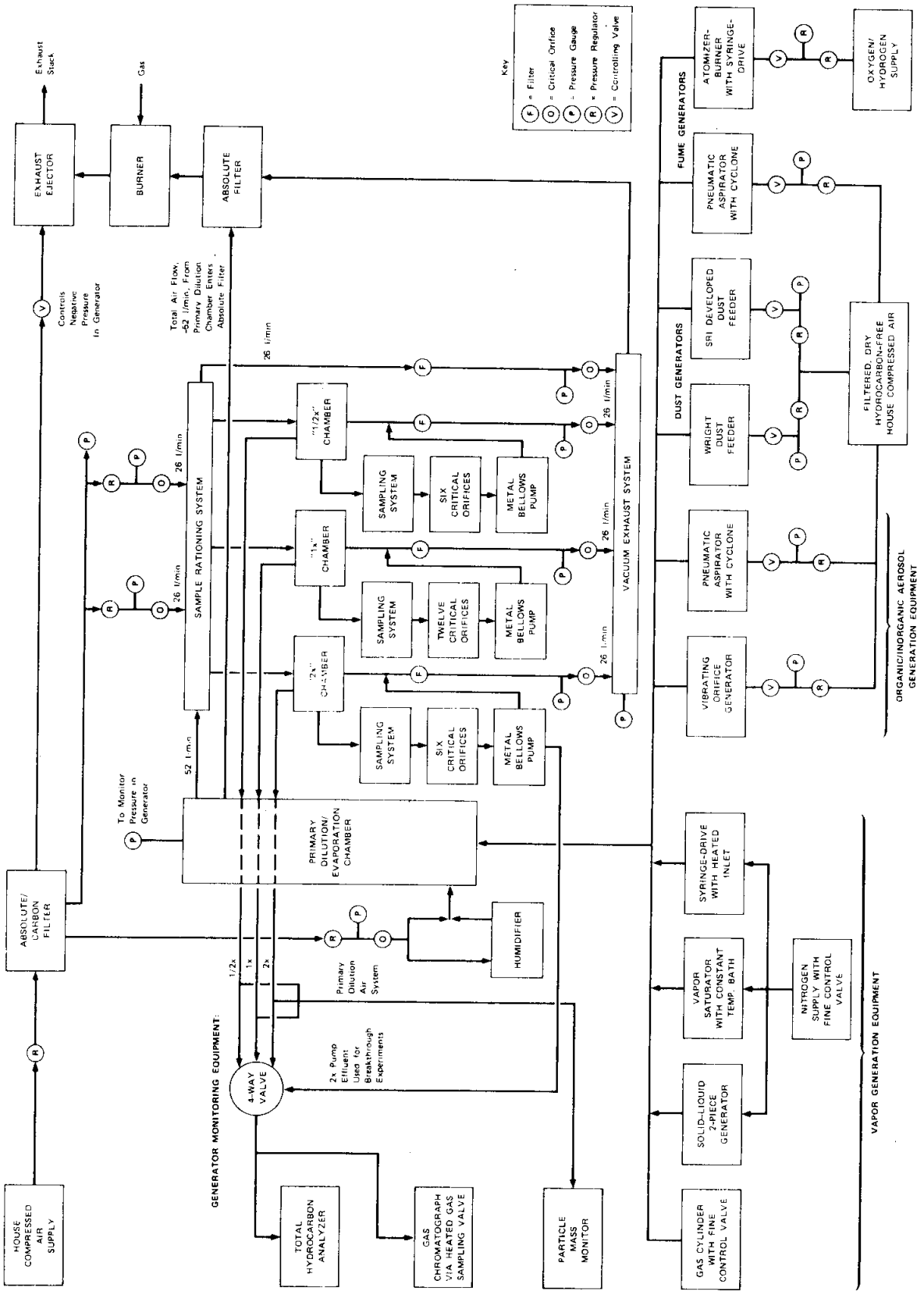


FIGURE S365-A1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

(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.

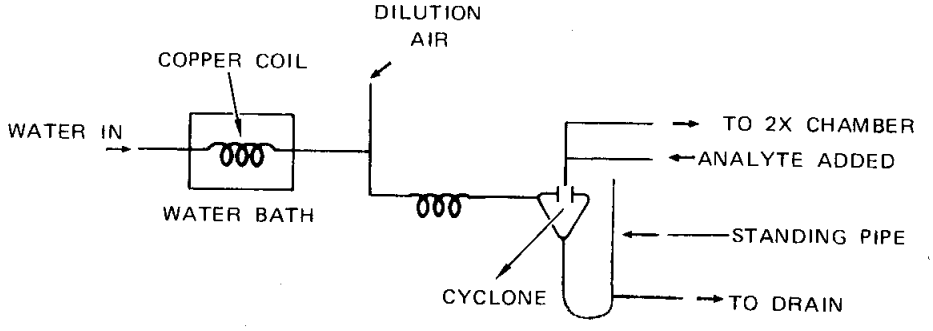
The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected 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 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 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.

Attachment C

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 S365-1 and S365-2. The vapor generator consists of two sections--a generating section (Figure S365-1) and a diluting section (Figure S365-2) which are connected by a ground glass joint.

The generating section (Figure S365-1) consists of a pyrex glass tube which is 2.4 cm in diameter and 19.5 cm long. A coarse glass frit is sealed in the bottom of the tube. The bottom of this tube is connected to a 7-mm O.D. glass tube which is bent 180° and extends up until it is nearly as high as the larger tube. The sample, which may be either a liquid or low melting solid, is introduced into the large tube. This part of the apparatus is immersed in a thermostated bath with the analyte level below the bath level. Nitrogen gas is introduced through the small tube and passes through the frit. The small bubbles, which form at the frit, rise through the liquid and become saturated or nearly saturated with the vapor of the liquid. The bath temperature and the flow of nitrogen determine the actual amount of vapor generated. Increasing either the nitrogen flow or the bath temperature, increases the amount of vapor generated.

The diluting section (Figure S365-2) of the vapor generator consists of a pyrex glass tube which is 2.4 cm in diameter and 13 cm high. The dilution air is introduced through a 7-mm O.D. glass tube connected to the side of the diluting tube. Sufficient air is added to dilute the vapor in nitrogen to the desired concentration. Vapor saturation of the air stream must not be exceeded to produce a well-mixed stream.*

The equations given in Reference No. 1 can be used to determine the approximate vapor concentration in the saturated nitrogen stream. The actual concentration of the vapor in each chamber in the generator should be measured using either a Beckman Model 402 total hydrocarbon analyzer or a gas chromatograph. Bag standards are used to calibrate the instrument used.

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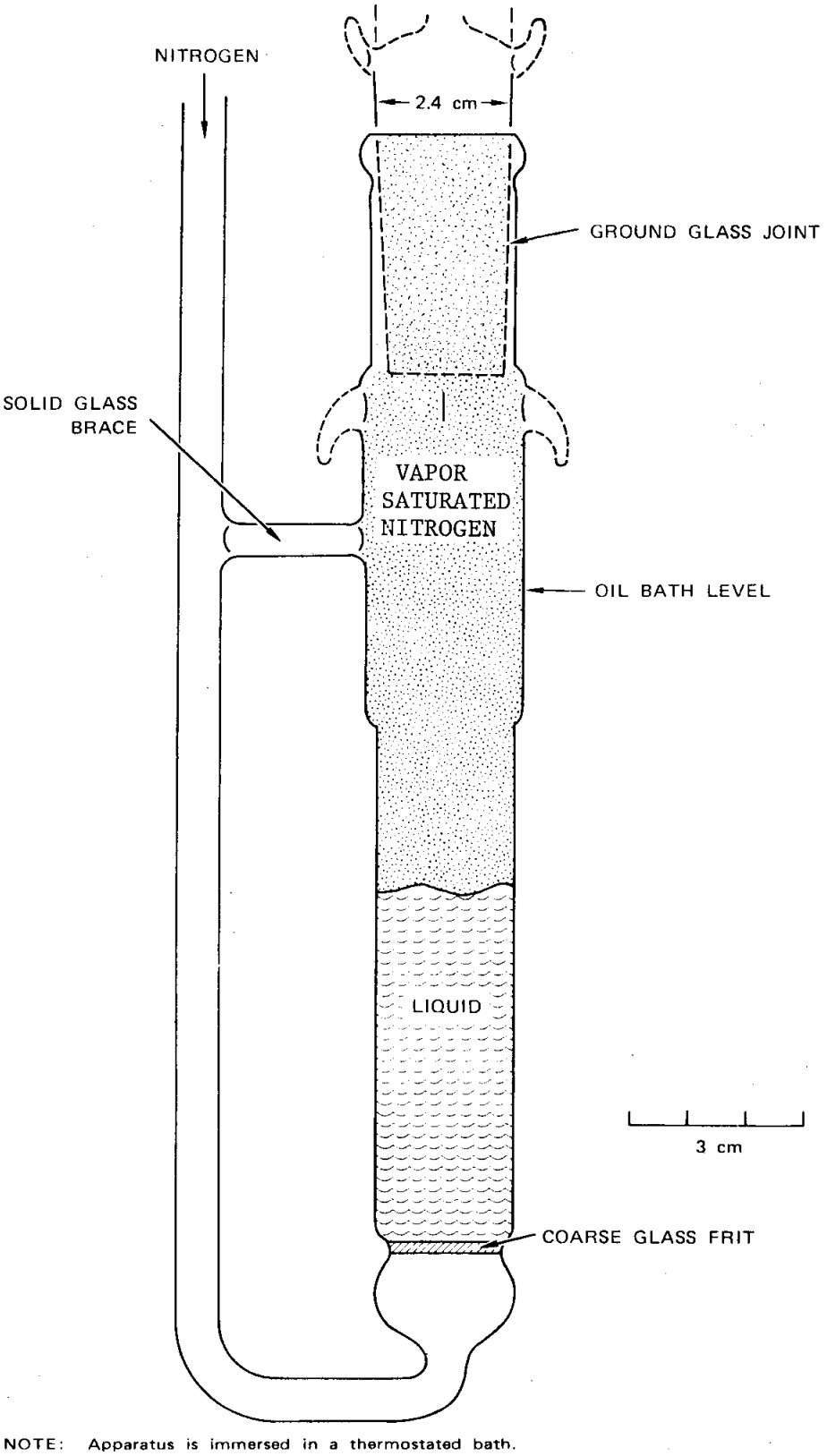
1. Physical Methods of Chemistry, Part V, A. Weissberger and B. W. Rossiter, eds., (John Wiley & Sons, 1971), 61-66.

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



NOTE: Apparatus is immersed in a thermostated bath.

FIGURE S365-C1 VAPOR GENERATOR (generating section)

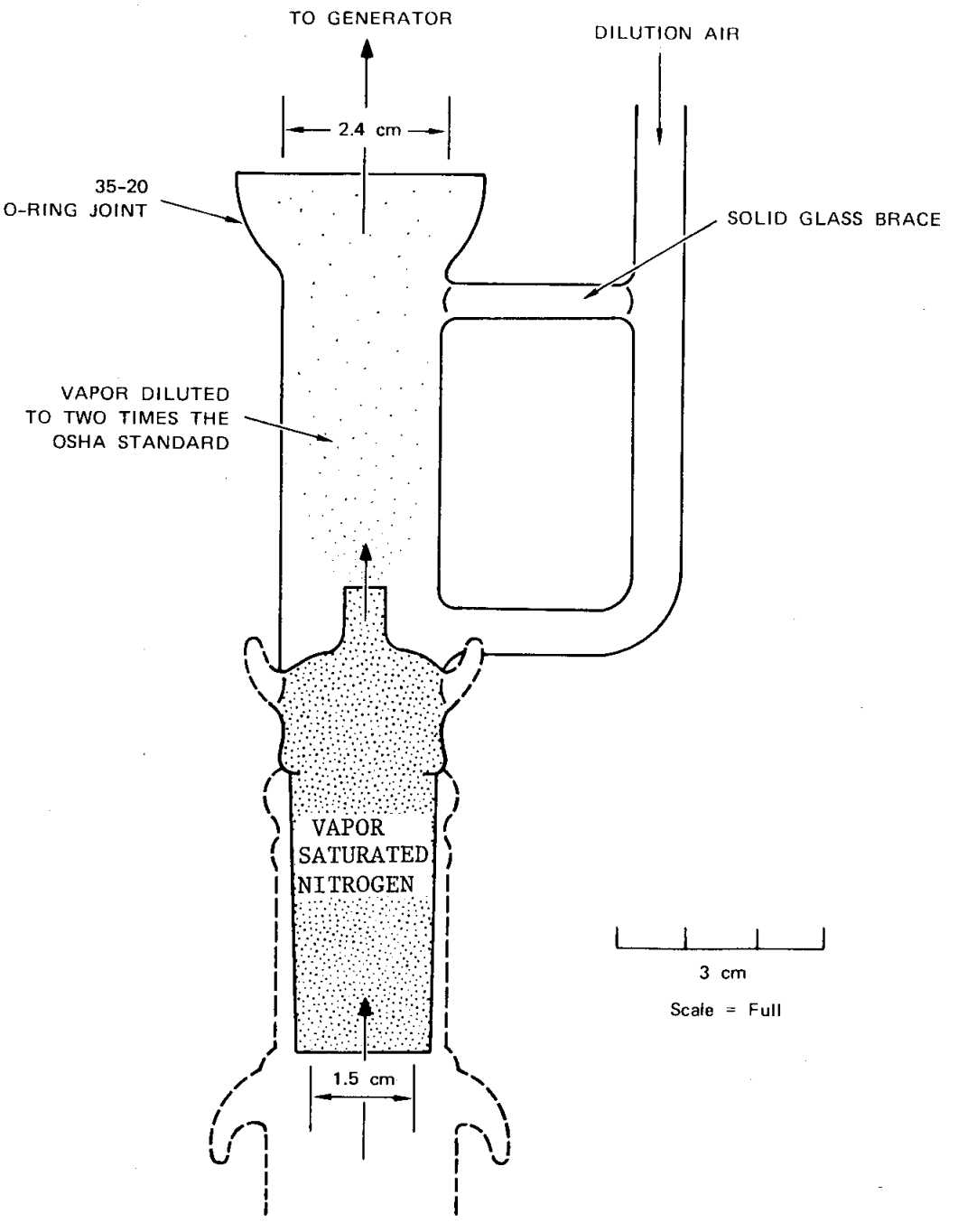


FIGURE S365-C2 VAPOR GENERATOR (diluting section)

Attachment D

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 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.

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

$\overline{CV}_2$ - 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.

$$\overline{CV}_S = \sqrt{(\overline{CV}_2)^2 - (\overline{CV}_1)^1}$$

$\overline{CV}_P$ - 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.

Analyte:	Hydroquinone	Method No:	S57
Matrix:	Air	Range:	0.84 - 4.05 mg/cu m
OSHA Standard:	2 mg/cu m	Precision ($\overline{CV}_T$):	0.061
Procedure:	Filter collection, extraction with aqueous acetic acid, HPLC	Validation Date:	11/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the hydroquinone aerosol present. This method is not applicable for sampling environments where significant hydroquinone vapor may be present.

1.2 Immediately after sample collection, the filter in the cassette is transferred into a jar and treated with aqueous acetic acid. Samples are stored and shipped in jars containing acetic acid solution.

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 290 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 0.84 - 4.05 mg/cu m at an atmospheric temperature and pressure of 20°C and 762 mm Hg, using a 90 liter sample. For a sample size of 90 liters the working range of the method is estimated to be 0.4 - 8.0 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution. The sensitivity of the analytical method is estimated to be at least 1.5 µg per ml.

3. Interference

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 0.84 - 4.05 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 11.2. Details of the test procedure are found in Reference 11.3.

4.2 A collection efficiency of at least 96% 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 99.4%. In addition, the samples were found to be stable when stored in the dilute acetic 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 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 One disadvantage is that some sample workup is required in the field to insure the stability of the sample. This step involves the transfer of the sample filter into a jar and addition of an aqueous solution of acetic acid.

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 the filter medium (Section 6.2) and 37-mm 3-piece cassette filter holder.

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 Ointment jars. Use squat form with Teflon film gaskets and screw cap for sample storage.

6.1.4 Graduated cylinder, 10 ml.

6.1.5 1% Aqueous acetic acid. Prepare a sufficient quantity for extraction and storage of samples.

6.1.6 Thermometer.

6.1.7 Barometer.

6.1.8 Stopwatch.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter. The filter is held in the three-piece cassette by a cellulose backup pad.

6.3 High Pressure Liquid Chromatograph equipped with a detector capable of UV detection at 290 nm.

6.4 Column (25 cm x 4.6 mm I.D. stainless steel) packed with Partisil™ 10-ODS, or equivalent.

6.5 Syringe, 100 µl, for HPLC injection.

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

6.7 Microliter syringes, 10-microliter and other convenient sizes for making standard solution.

6.8 Volumetric flasks, 25-milliliter and other convenient sizes for making standard solutions and sample dilutions.

7. Reagents

7.1 Hydroquinone, reagent grade.

7.2 Distilled water.

7.3 Glacial Acetic acid.

7.4 Acetic acid in distilled water, 1%. Prepare by diluting

10 ml of glacial acetic acid to 1000 ml with distilled water. This solution is used for sample extraction and all dilutions and also as the mobile phase for the HPLC analysis.

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 cassette 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 cassette 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 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.4 Turn the pump on and begin sample collection. 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 observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.6 Open the cassette filter holder. Carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers and transfer filter to the 2-oz. ointment jar.

8.3.7 Add 10-ml of 1% acetic acid into the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

8.3.8 Shipping. The ointment jars should be shipped in a suitable container, designed to prevent damage and leakage in transit.

8.3.9 Blank. 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.

8.3.10 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.

8.4 Analysis of Samples

8.4.1 Preparation of samples:

1. Transfer the sample solution to a 25 ml volumetric flask.

2. Rinse at least twice with 5 ml of 1% acetic acid and add the washings to the volumetric flask.

3. Make volume up to 25 ml with 1% acetic acid.

8.4.2 Analysis by high pressure liquid chromatograph. The mobile phase is 1% acetic acid. The typical operating conditions for the liquid chromatograph are:

1. 1.0 ml/min solvent flow rate

2. Ambient column temperature

3. 400-600 psi system pressure

8.4.3 Injection. The first step in the analysis is the injection of the sample into the liquid chromatograph.

A 100 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 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 a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter with 10-ml of 1% acetic acid in a jar, 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 the method, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level was used to determine the analytical method recovery. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) were spiked. A parallel blank filter is also prepared except that no sample is added to it. All filters were then extracted and analyzed as described in Sections 8.3.7 and 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

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

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

9.1 Hydroquinone stock solution, 90 µg/25 µl. Dissolve 0.0900 g of hydroquinone in 25 ml of 1% acetic acid. Prepare a fresh solution daily.

9.2 From the stock standard solution, prepare at least 6 working standards to cover the concentration range of 90-360 µg/25 ml. Transfer 25 to 100 µl aliquots of the stock standard into 25-ml volumetric flasks and dilute to volume with 1% acetic acid.

9.3 These series of standards are analyzed under the same HPLC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in micrograms per 25.0 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/25 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 25.0 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 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 (^{o}K)
T_2 = temperature of air sampled (^{o}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, NIOSH Contract No. CDC-99-74-45.

11.2 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."

11.3 S57 Backup Data Report for Hydroquinone, prepared under NIOSH Contract No. 210-76-0123, 11/26/76.

Sampling Data Sheet No. S57

Substance

Hydroquinone

Standard

8-hour time-weighted average: 2.0 mg/cu m

Analytical Method

A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the hydroquinone particulate present. The sample filters are stored in 1% acetic acid and the solution is analyzed by high pressure liquid chromatography using a variable wavelength UV detector set at 290 nm. The method has been validated over a concentration range of 0.84 - 4.1 mg/cu m at 20°C and 762 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The following equipment is needed for sampling hydroquinone 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 cassette filter holder held together by tape or shrinkable band; a 37-mm/0.8 micrometer mixed cellulose ester membrane filter (MCEF) supported by a cellulose backup pad; a 2 oz. ointment jar sealed with Teflon film and cap or any other suitable container capable of storing the cellulose filter and 10 ml of solution; a 1% acetic acid in distilled water solution; and a 10-ml graduate or any other device capable of adding roughly 10 ml of solution to the filter container.

Sample Size

A sampling period of one hour is recommended. Sample at a flow rate of 1.5 liters per minute.

Sampling Procedure

1. Assemble the filter and three-piece filter cassette and close firmly to insure that the center ring seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

2. Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3. Air being sampled should not be passed 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 all the necessary information to determine flow rate or volume and record also the initial and final sampling time. 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 flow rate cannot be adjusted to correct a problem, terminate the sampling.

5. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 2-oz. ointment jar. The filter should lay flat at the bottom of the jar.

6. Add 10 ml of 1% acetic acid to the ointment jar and seal using Teflon film as a gasket.

7. Carefully record sample identity and all relevant sample data.

8. Blank. 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 hydroquinone 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 containers in which the sample filter and acetic acid are stored should be shipped in a suitable container designed to prevent damage or leakage in transit.

Reference

Hydroquinone, NIOSH Method No. S57.

Backup Data Report No. S57

Substance: Hydroquinone

OSHA Standard: 2.0 mg/cu m

Chemical Used for Validation: Hydroquinone, J. T. Baker Chemical Co., 99%

General Considerations

The method for hydroquinone 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 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 hydroquinone consisted of the following experimental studies:

- Developed two high pressure liquid chromatographic systems based on normal phase and reversed phase chromatography; these chromatographic systems, which allow the resolution of hydroquinone from quinone, were used in conjunction with studies associated with finding ways to stabilize the collected hydroquinone samples.

- Analyzed a total of 18 analytical samples (6 samples at each of three test levels for a 90-liter sample) prepared by adding known amounts of hydroquinone to 37-mm Type AA Millipore filters, 0.8 micrometer pore size.

- Analyzed a set of 18 samples (6 samples at each of the three test levels) collected from dynamically generated test atmospheres at 0.5, 1 and 2X the TWA concentration for a 90-liter sample.

- Determined the collection efficiency on mixed cellulose ester membrane filter.

- Tested the storage stability of collected samples.

- Assessed 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 and Ways to Stabilize Samples

On the basis of preliminary experimental studies conducted under this program (i.e., no sample loss was observed when room air was passed through spiked filters at 1.5 liters per minute for 60 minutes), hydroquinone would exist as a particulate at the test levels of interest. Thus, the analytical method evaluated primarily consisted of extracting the hydroquinone from the filter using a compatible solvent and analysis of the extracted sample by high-pressure liquid chromatography (HPLC) using either of the two chromatographic systems developed. Note that the development of two chromatographic systems was a by-product of the need to stabilize the hydroquinone samples after sample collection.

A. Chromatographic Systems

During the course of these validation studies, several chromatographic systems were screened relative to their applicability to the hydroquinone analysis. A summary of these chromatographic systems, together with the solvent used to extract the hydroquinone from the filter, are listed in Table S57-1. Note that in each case the extracting solvent was chosen based on hydroquinone solubility and compatibility with the HPLC solvent system in order to optimize the chromatographic resolution.

Of the various normal and reversed phase chromatographic systems tested, two combinations proved to give the most satisfactory resolution--normal phase chromatography on Partisil 10 with 10% ethyl acetate in chloroform and reversed phase chromatography on Partisil 10-ODS with 1% glacial acetic acid in water. The details of the chromatographic conditions used for each of these two combinations are summarized in Table S57-2. In either of these chromatographic systems, hydroquinone is resolved from quinone except that in the normal phase system, quantitation of quinone is not possible because the solvent peak interferes. Although quinone is a vapor which would not be collected on a filter, it was felt to be desirable to be able to quantitate quinone so that it could be correlated with any loss of hydroquinone via oxidation to quinone.

B. Ways to Stabilize Collected Hydroquinone Samples

Hydroquinone samples were collected on 37-mm Type AA Millipore filters from dynamically generated test atmospheres as described in the Sampling and Analysis section. Several sets of samples were collected and stored under the following storage conditions:

1. As collected, in the properly sealed and plugged cassettes.

2. Flushed with nitrogen after sampling and stored in cassettes in a nitrogen atmosphere.

3. Stored in aqueous ascorbic acid.

4. Stored in aqueous acetic acid.

Table S57-1

Summary of Chromatographic Conditions Tested[1]

Chromatographic Solvent	Extracting Solvent	Column[2]
Methanol/$CHCl_3$ (gradients and mixtures)	Isopropanol/Methanol (1:1)	Partisil 10
Ethyl Acetate/$CHCl_3$ (gradients and mixtures)	Isopropanol/Methanol (1:1)	Partisil 10
10% Ethyl Acetate in $CHCl_3$	Methanol/10% Ethyl Acetate in $CHCl_3$ (1:9)	Partisil 10
100% H_2O	H_2O	Partisil 10-ODS
1% glacial acetic acid in water	1% glacial acetic acid in water	Partisil 10-ODS
1% glacial acetic acid in water	Ascorbic acid in water, 260 mg/liter	Partisil 10-ODS

[1] The chromatographic response was monitored simultaneously at 254-nm and 290-nm; only the 290-nm wavelength was found to be useful.

[2] Stainless steel, 25-cm x 4.6-mm I.D. packed with the designated 10-micron column packing. Partisil is a trade mark for the microparticle silica marketed by Whatman-Reeve Angel.

Table S57-2

Summary of Chromatographic Systems Used

	Normal Phase	Reversed Phase
HPLC Column	Partisil 10	Partisil 10-ODS
HPLC Solvent	10% Ethyl acetate in chloroform	1% Glacial Acetic Acid in water
Solvent Flow rate	2 ml/min	1 ml/min
Extracting Solvent	Methanol/HPLC Solvent (1:9)	HPLC Solvent
Hydroquinone Retention time	245 seconds	310 seconds
Detector wavelength	290 nm	290 nm

The samples stored under conditions 1 and 2 were analyzed by normal phase chromatography while the samples stored in acidic aqueous media were analyzed by reverse phase chromatography. The storage stability tests were conducted such that six replicate samples at a test concentration level were collected simultaneously. These six samples were split into two sets of 3 samples each--three samples were analyzed after 1 day (less than 24 hours) and the other three were stored for 7 days prior to analysis. The data for these storage tests are summarized in Table S57-3. Sample stability was measured in terms of the relative ratios found for the 7-day-old samples vs. the 1-day-old samples.

The data in Table S57-3 may indicate that the first two storage conditions do not favor sample stability particularly at the higher test concentration such as 2X the OSHA standard test level. The analytical method recovery (extraction with methanol/ethylacetate-$CHCl_3$ and normal phase HPLC analysis) used for these storage studies was 97.5% with a Coefficient of Variation equal to 0.051. (Refer to Table S57-4). Storage of collected samples in dilute ascorbic acid solution was equally unsatisfactory indicating hydroquinone losses of 11 to 18% over a 7-day period. It was observed that the samples which showed hydroquinone losses also showed a corresponding increase of the quinone peak.

The samples stored in aqueous acetic acid immediately after collection showed no loss of hydroquinone after 7 days storage. This storage condition was adapted for all subsequent analyses and is the recommended method for hydroquinone.

Principle of the Method

The method validated for the analysis of hydroquinone in air is based on collection on mixed cellulose ester membrane filter, recovery from the filter by acetic acid extraction and analysis by high pressure liquid chromatography. The samples must be stored in the acetic acid solution after sample collection in order to maintain sample stability.

Analysis

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. S57 (Reference 4).

The reliability of the analytical method was tested based on the analysis of 18 filter samples. The analytical samples were prepared by spiking 37-mm Type AA Millipore filters with known aliquots of hydroquinone in an aqueous 1% acetic acid solution. The aliquots added contained respectively 91, 182 and 364 micrograms of hydroquinone representing the equivalent of a 90-liter air sample at 0.5, 1 and 2X the OSHA standard.

Each filter was placed in a 2-oz. ointment jar and immediately treated with 10 milliliters of 1% aqueous acetic acid. The jars were sealed

Table S57-3

Effect of Storage Condition on Stability of Hydroquinone
Samples Collected on Type AA Millipore Filters

A. Samples stored in sealed cassettes as collected.

mg/cu m Found*		Ratio
Stored 1 day	Stored 7 days	(7 days: 1 day)
0.862	0.821	0.952
1.238	1.138	0.919
1.937	1.979	1.022
2.343	2.318	0.989
4.82	4.11	0.853

B. Samples Flushed with Nitrogen and Stored in Nitrogen Atmosphere.

mg/cu m Found*		Ratio
Stored 1 day	Stored 7 days	(7 days: 1 day)
2.356	2.320	0.985
4.86	4.25	0.874

C. Samples Stored in Aqueous Ascorbic Acid (260 mg/liter, pH 3.2).

mg/cu m Found*		Ratio
Stored 1 day	Stored 7 days	(7 days: 1 day)
0.705	0.630	0.894
1.739	1.423	0.818
4.27	3.48	0.815

D. Samples Stored in Aqueous Acetic Acid (pH 2.7).

mg/cu m Found*		Ratio
Stored 1 day	Stored 7 days	(7 days: 1 day)
0.601	0.669	1.113
1.356	1.407	1.038
2.992	2.962	0.990

*Each value reported is the average of at least three samples.

Table S57-4

Data Sheet: Hydroquinone

Analysis*

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
92.2	90.3	0.979	179.5	177.7	0.990	356	346	0.972
92.2	93.7	1.016	179.5	172.4	0.960	356	386	1.084
92.2	85.5	0.927	179.5	155.4	0.866	356	371	1.042
92.2	90.9	0.986	179.5	187.4	1.029	356	366	1.028
92.2	86.0	0.933	179.5	166.1	0.925	356	351	0.986
92.2	87.3	0.946	179.5	155.8	0.868	356	359	1.008
n =	6			6			6	
mean		0.965			0.940			1.020
std dev		0.0348			0.0659			0.0406
CV_1		0.0361			0.0701			0.0398

$$\overline{CV}_1 = 0.0510$$

$$\overline{CV}_{A+\overline{AMR}} = 0.0514$$

* These samples were analyzed using the normal phase chromatographic system. (Table S57-2)

with a screw cap and Teflon film gasket and were stored overnight. Each sample solution was then transferred to a 25 ml volumetric flask, the ointment jars were rinsed with 1% acetic acid at least twice and added to the flask and the sample was made up to volume. The data for the full set of 18 samples analyzed by reversed phase chromatography is given in Table S57-5.

The instrumentation used for the analysis of hydroquinone was a Waters Associates ALC 200 series Liquid Chromatograph equipped with a Model 6000A Solvent Delivery System, a Model 660 Solvent Programmer, a Model 440 Absorbance Detector (254 nm), and a Model U6K Injector. It is also equipped with a variable wavelength detector, a Schoeffel Instrument Corporation Spectroflow Monitor SF770 in combination with Schoeffel Instrument Corporation GM 770 Monochromator. The UV absorbance was monitored at 290 nm. A Spectra Physics Autolab System I Computing Integrator was used for all peak area measurements.

Sampling and Analysis

Particulate hydroquinone was generated using the basic Aerosol Generation/Dilution/Sampling System described in detail in Attachment A. 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 hydroquinone containing 29.0 grams of hydroquinone per liter 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 84 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 6 samples at the three test levels were collected simultaneously at 1.5 liters per minute for 60 minutes (90 liters). The 18 samples were analyzed as described in NIOSH Method No. S57 and the data are summarized in Table S57-6.

Studies were also conducted to determine the particle size distribution of the hydroquinone 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 hydroquinone deposited at each stage by extraction with 1% acetic acid and analysis by HPLC.

The data obtained by HPLC analysis of the hydroquinone collected at each stage of the cascade impactor are tabulated below. The effective cut-off 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.

Table S57-5

Data Sheet: Hydroquinone

Analysis*

Level	0.5S		1S			2S		
	µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
	91.0	88.3	0.970	182.1	173.5	0.953	364	376	1.033
	91.0	88.1	0.968	182.1	180.7	0.992	364	363	0.997
	91.0	91.5	1.005	182.1	185.4	1.018	364	373	1.025
	91.0	94.0	1.033	182.1	179.3	0.985	364	369	1.014
	91.0	85.0	0.934	182.1	179.0	0.983	364	366	1.005
	91.0	93.2	1.024	182.1	181.7	0.998	364	347	0.953
n =	6			6			6		
mean		0.989			0.988			1.005	
std dev		0.0381			0.02133			0.02840	
CV_1		0.0385			0.02159			0.02827	

$$\overline{CV}_1 = 0.0303$$

$$\overline{CV}_{A+\overline{AMR}} = 0.0327$$

*These samples were analyzed using the reversed phase chromatographic system (Table S57-2).

Table S57-6

Data Sheet: Hydroquinone
Sampling and Analysis

Test Level	Found			Taken*	
	µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	78.3	90.4	0.866	0.767	
	74.1	90.1	0.822	0.767	
	73.0	89.8	0.813	0.767	
	76.8	90.3	0.850	0.767	
	78.7	90.0	0.874	0.767	
	72.6	90.8	0.800	0.767	
		n = 6			
		mean	0.838		1.092
		std dev	0.0302		
		CV_2	0.0360		
1S	169.2	90.5	1.870	1.800	
	170.0	90.7	1.874	1.800	
	155.3	90.2	1.722	1.800	
	165.7	90.9	1.822	1.800	
	165.2	91.3	1.809	1.800	
	166.5	90.8	1.834	1.800	
		n = 6			
		mean	1.822		1.012
		std	0.0554		
		CV_2	0.0304		
2S	374	90.5	4.13	3.93	
	351	90.4	3.88	3.93	
	387	90.5	4.28	3.93	
	362	90.4	4.00	3.93	
	360	90.2	3.99	3.93	
	368	91.2	4.04	3.93	
		n = 6			
		mean	4.05		
		std dev	0.1374		1.033
		CV_2	0.0339		
		$\overline{CV}_2$	0.0335		

* Based on UV analyses of two samples at each level.

Stage	Particle Size Range Cut-off Diameter (µm)	µg Hydroquinone Found	% Total Particulate	Cumulative %
1	4.7 and up	5.03	0.7	100.0
2	<4.7 - 3.3	7.16	1.0	99.3
3	<3.3 - 2.1	13.58	2.0	98.3
4	<2.1 - 0.65	127.2	18.5	96.3
Backup Filter	<0.65	536	77.8	77.8
	TOTAL	689		

Storage Stability

Studies were done to assess the stability of hydroquinone samples collected on mixed cellulose ester membrane filter and stored for 7 days in 10 ml of 1% glacial acetic acid. The samples were stored in ointment jars at ambient conditions. For these studies, a set of 18 samples was collected from a dynamically generated test atmosphere. Nine of these samples (3 at each of the three test levels) were treated with 1% glacial acetic acid immediately after collection and analyzed as described in Section 8.4 of NIOSH Method No. S57 after overnight storage. The other 9 samples were also treated with 10 ml of glacial acetic acid immediately after collection, stored for 7 days and analyzed similarly. The data for these samples are shown in Table S57-7 and indicate that the hydroquinone samples are stable when stored in dilute acetic acid solution. The average recovery over the three test levels was 97% for the one-day-old samples vs 101.5% for the seven-day-old samples.

Collection Efficiency

The collection efficiency of 37-mm Type AA Millipore filters for hydroquonone was determined by collecting six filter samples at a test concentration of 4.05 mg/cu m for a 90 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 100.0% (or at least 96.2%) at the 2S test concentration studied as indicated by the data summarized in Table S57-8.

On the basis of extrapolating available data, the vapor pressure of hydroquinone has been estimated to be 0.0042 mm of Hg at 25°C (Reference 5). In another article (Reference 3) the vapor pressure has been reported to be 0.000018 Torr at 25°C. In order to confirm whether hydroquinone vapor exists or whether hydroquinone vaporization losses can occur during sampling, additional experiments were carried out. A set of six filters were spiked with 720 micrograms of hydroquinone to

Table S57-7

Data Sheet: Hydroquinone

Studies in Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found			Taken*	
	µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	52.0	91.8	0.566	0.634	
	59.7	91.5	0.652	0.634	
	54.0	92.3	0.585	0.634	
		Mean	0.601		
		CV_2	0.0752		0.948
1S	124.2	92.4	1.344	1.391	
	127.5	92.8	1.374	1.391	
	124.7	92.3	1.351	1.391	
		Mean	1.356		0.975
		CV_2	0.0116		
2S	269.0	91.9	2.927	3.03	
	277.0	91.8	3.02	3.03	
	280.7	92.7	3.03	3.03	
		Mean	2.992		0.987
		CV_2	0.0190		

Expt. B: Samples Stored 7 Days

0.5S	62.5	91.9	0.680	0.634	
	58.7	91.6	0.641	0.634	
	62.7	91.3	0.687	0.634	
		Mean	0.669		1.056
		CV_2	0.0371		
1S	127.3	92.1	1.382	1.391	
	135.0	92.2	1.464	1.391	
	126.2	91.7	1.376	1.391	
		Mean	1.407		1.012
		CV_2	0.0349		
2S	275.5	92.1	2.991	3.03	
	269.5	91.9	2.933	3.03	
	Sample Lost				
		Mean	2.962		0.978
		CV_2	0.0138		

* Calculated from direct UV analysis of 2 samples at each level.

Table S57-8

Collection Efficiency of Hydroquinone on Type AA Millipore Filters

Sample Size: 90 liters at 4.05 mg/cu m*

µg Found			% Collected
Front	Backup	Total	in front
374	N.D.	374	100
351	N.D.	351	100
387	N.D.	387	100
362	N.D.	362	100
360	N.D.	360	100
368	N.D.	368	100

Average Collection Efficiency.... 100**

N.D. = Not detectable; the detection limit was 14 µg per 10 ml.

* The test concentration noted is based on the average found for the six samples at the 2X level.

** The average collection efficiency can also be expressed as at least 96.2% on the basis of the detection limit and the average µg found on the front filter.

represent a two-hour collection at 2X the OSHA standard. Through three of these filters, 180 liters of room air was sampled at 1.5 liters/min. The three samples were then analyzed by HPLC, together with the other three spiked filter samples through which no air was passed. A mean recovery of 106.2% was obtained for the three samples exposed to 180 liters of air vs 103.1% for the other three filters. The data shows no significant loss through vaporization and indicates that hydroquinone is a particulate at the test concentrations of interest. It is also noted, however, that at higher temperatures or in operations where hydroquinone vapor may exist, this method would not be functional and an alternate collection method should be used.

Independent Method of Verifying Generator Concentration

The concentration of hydroquinone particulate produced by the aerosol generation/dilution system was verified by the analysis of two generated samples at each test level by direct UV spectrophotometry. This analysis was done by preparing an independent calibration curve based on six calibration standards. Absorbance measurements were done at 290 nm using a Perkin-Elmer Coleman 55 Spectrophotometer and a 1-cm path length cell. The "taken" concentration shown in Tables S57-6 and S57-7 were obtained based on the UV analysis of duplicate filter samples.

The data for the six samples used to determine the "taken" concentration shown in Table S57-6 is shown below and compared with the averages found by HPLC analysis.

	Taken mg/cu m Based on Direct UV Analysis		
	0.5S	1S	2S
	0.809	1.803	3.99
	0.726	1.797	3.88
Average Taken (Direct UV Analysis)	0.767	1.800	3.93
Average Found (HPLC Analysis)	0.838	1.822	4.05

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and summarized in Attachment B.

The precision of the analytical method was assessed using the data in Table S57-5. The pooled Coefficient of Variation ($\overline{CV}_1$)for three sets of analytical samples was found to be 0.030.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S57-6 and the results obtained from collection efficiency and storage stability tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from dynamically generated test atmospheres is 0.034. To obtain a measure of 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 latter was determined as described in the section on independent method of verifying generator concentration.

The average recovery (concentration found divided by concentration taken) for all three levels was 104.5%. 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 above.

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for hydroquinone. The data (Table S57-6) gave a chi squared value of 0.12, 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 total Coefficient of Variation ($\overline{CV}_T$) is 0.061.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, U.S. Government.

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. Coolidge, A. S., and Coolidge, M. S., J. Am. Chem. Soc., 49, (1927).

4. Hydroquinone, NIOSH Method No. S57, prepared under NIOSH Contract No. 210-76-0123, with validation date 11/26/76.

5. Jordan, Earl T., "Vapor Pressure of Organic Compounds," Interscience Publishers, Inc., New York, 90, (1954).

Attachment A

AEROSOL GENERATION/DILUTION/SAMPLING SYSTEM

The aerosol dilution and sampling system is shown schematically in Figure S57-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. Figure S57-A-2 shows the latter sections in more detail.

Aerosol dilution ratios in the system are fixed by the action of critical flow orifices. Usually an aerosol with a concentration twice the OSHA standard is prepared in the mainline, and this aerosol sampled without dilution in one dilution/sampling section and diluted twofold and fourfold in the other two sections. Other dilution modes may be accommodated simply by changing the critical orifices. There are six sample ports on each section. There is a luer fitting on each sample port to mate with a Millipore filter cassette. Sampling flowrates are controlled by six critical orifices located on each sample manifold.

A number of different aerosol generators including a pneumatic atomizer, an ultrasonic nebulizer, and a dust disperser may be used in conjunction with the dilution and sampling system.

Aerosol Generation

The following aerosol generation equipment is available for use with the system:

- Environmental Research Corporation Fluid Atomization Aerosol Generator Model 7330
- DeVilbiss Model 35A Ultrasonic Nebulizer
- Royco Model WA Aerosol Generator
- Wright Dust Feeder

The ERC and DeVilbiss generators are used to produce aerosols by spray drying or by atomization of suspended solid particles. For spray drying, the material to be dispersed is dissolved in an appropriate solvent, the solution atomized, and the resulting mist mixed with solvent-free air. The solvent evaporates and leaves the nonvolatile solute behind as a residue. Either solid or liquid solutes may be used. Aerosols with median diameters in the 0.03 to 0.5 micron particle size range may be prepared by spray drying with the ERC atomizer. Slightly larger particles may be prepared by spray drying from the DeVilbiss unit. Both aerosol concentration and particle size are functions of the concentration of solute in the atomized solution.

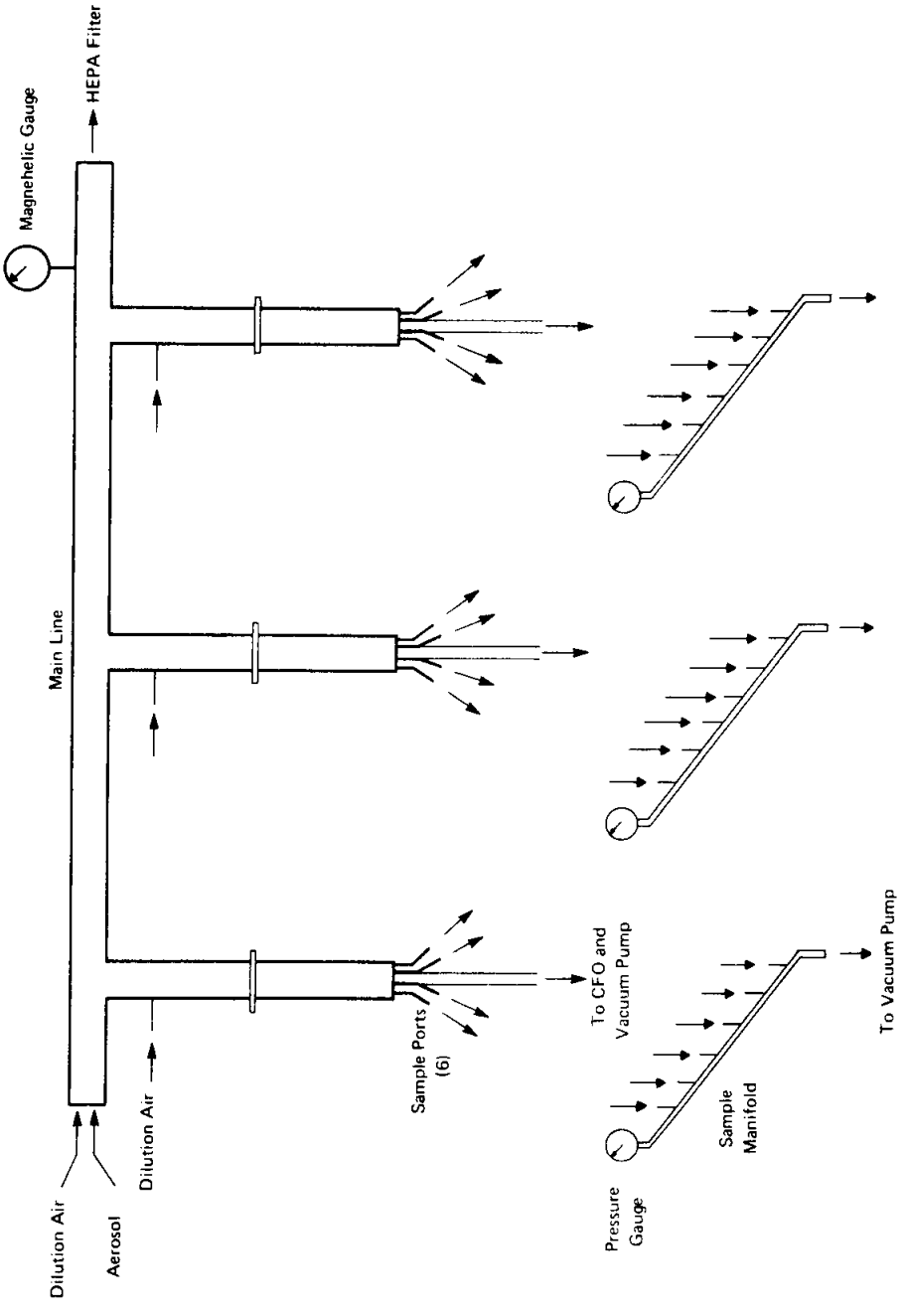


Figure S57-A-1 Aerosol Dilution and Sampling System

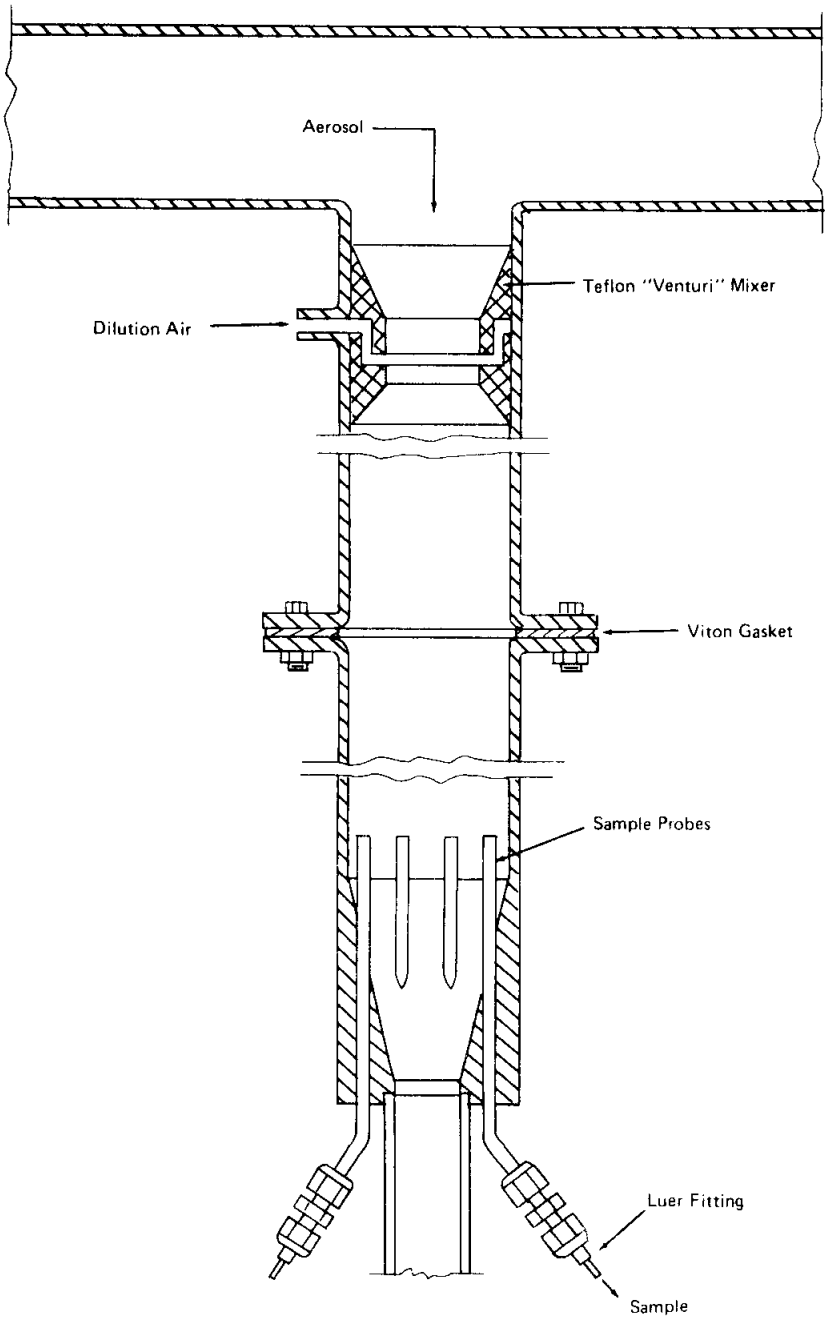


Figure S57-A-2 Cross-Sectional View of Dilution and Sampling Section

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 micrometer.

The Wright Dust Feeder is used to disperse powders. Samples to be dispersed in the apparatus are compressed into a special holder. In operation, the holder and the dust compact are slowly rotated and driven against a stationary scraper blade which continuously removes dust from the compact surface at a uniform rate. The rate of dust delivery from the feeder may be varied by changing gears in the compact advance mechanism. The powder is entrained in an air stream and is dispersed by impaction on a metal plate. Ideally the size distribution of the particles in the dust cloud should be governed by the particle size distribution of the original powder, however, in practice it is usually difficult to disperse a powder completely. Agglomerates are often formed.

Air Supply

Air from the house compressed air system is treated by successive passage through a cotton filter, a silica gel bed, a high efficiency glass fiber filter, and a membrane filter. These remove respectively, oil and water droplets, water vapor, and fine particles.

The treated air then passes to two parallel air supply manifolds, each of which is equipped with valves for controlling air flow to various parts of the generation/dilution system. One of the manifolds supplies air to the dilution system. The second supplies air to the aerosol generator, either directly or through calibrated rotameters as may be required by the particular generator being used. Pressure in each manifold is maintained at a fixed level by Moore Nullmatic pressure regulators and is measured with bourdon gauges (6" Ashcroft test gauges).

Dilution and Sampling Sections

Aerosol dilution occurs in the Teflon venturi-shaped inserts shown in Figure S57-A-2. Dilution air is injected radially into the venturi throat. The quantity of dilution air introduced is fixed by a critical orifice which is connected to one of the constant pressure air manifolds.

Six isokinetic sampling probes are located approximately thirty centimeters downstream of each diluter. The probes convey aerosol to sample collectors (filter cassettes) mounted radially around the outside

of the sampling section. Sample flowrate is fixed at 1.5 liters per minute by critical orifices (sapphire orifices supplied by Richard H. Bird and Co., Waltham, Mass.) mounted on the sample manifold (Figure S57-A-1).

As is indicated in Figure S57-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. There are seven outwardly flowing streams in each branch--one stream is that which flows through the orifice mentioned above (flowrate Q_T) and the other six are the sample streams (total flowrate Q_S). There are two inflowing streams--the dilution air stream (flowrate Q_D) and the aerosol stream entering from the main line (flowrate Q_A). The dilution ratio, R, in each branch is given by:

$$\frac{Q_A}{Q_A + Q_D}$$

or since $Q_T + Q_S = Q_D + Q_A$ (with the assumption of uniform pressure and temperature in the system),

$$R = \frac{Q_T + Q_S - Q_D}{Q_T + Q_S}$$

The flowrates, Q_T, Q_S and Q_D are controlled by the action of critical orifices; consequently the dilution ratios are fixed solely to flow through the critical orifices.

Dilution ratios are measured by adding a small quantity of hydrocarbon gas to the main line and measuring the relative concentrations in each of the three sampling sections using a Beckman 402 hydrocarbon analyzer. Dilution ratios of 1.00 to 0.488 to 0.241 are typical when the system is set to generate a 2X OSHA standard concentration in the main line. No measurable differences (within 1%) in the hydrocarbon concentration were found among the six sample ports on any of the three sampling ports. The dilution ratios are rechecked periodically.

The main line flowrate is about 150 liters per minute when a 2X OSHA standard concentration is being generated in the main line. Flow through the dilution/sampling branches is approximately 70 liters per minute.

Excess aerosol from the main line is passed through a HEPA filter and then vented to a hood.

Experimental Procedure

1) The aerosol generator parameters necessary to produce the desired aerosol concentration are found by making several trial runs. If the

spray drying procedure is being used, the concentration of the atomizer solution would be varied in the trial runs. If the dust feeder were being used, the sample feed rate would be varied.

2) Six samples, each consisting of two filters sampling in series are taken from the 2X OSHA standard sampling ports to verify that the collection efficiency of the filters is adequate.

3) A full set of eighteen samples are collected simultaneously.

Typical System Parameters

When the dilution/sampling system is set up to produce aerosols with a 2X OSHA standard concentration in the main line, typical values of the system parameters are:

Main line pressure:	+ 3 cm H_2O with respect to atmospheric pressure
Main line flowrate:	150 liters per minute
Sampling rate:	1.5 liters per minute
Flowrate through dilution/ sampling branch (approximate):	68 liters per minute

Dilution air flowrate (approximate):

2X OSHA standard branch	0
1X OSHA standard branch	36
0.5X OSHA standard branch	53

Dilution ratios (measured with hydrocarbon analyzer):	1.00:0.488:0.241

Attachment B

SUMMARY OF STATISTICAL TERMS AND FORMULAE

The statistical analysis employed in this program has been provided by NIOSH. The evaluation of the limits and guidelines are discussed in a series of memoranda from Busch (Reference A). Some key terms, statistical formula, acceptable limits and statistical tests which have been used in these reports are noted and summarized herein.

Mean - Arithmetic mean or average, defined as the sum of all the observations divided by the number of observations (n).

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

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

CV - Coefficient of Variation or Relative Standard Deviation, defined as the standard deviation divided by the mean.

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

CV_1 - Coefficient of Variation for the six analytical samples at each of the 0.5, 1, and 2X OSHA standard level.

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

$\overline{CV}$ - Pooled Coefficient of Variation; in this program, the value is derived from the coefficients of variation obtained from the analysis of 6 samples at each of the three test levels - 0.5, 1 and 2X OSHA standard level. The mathematical equation is expressed as:

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

where:

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

CV_i = Coefficient of Variation of the observations at the i^{th} level

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

$\overline{CV}_1$ - Pooled Coefficient of Variation calculated as above based on data for the 18 analytical samples

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

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

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

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

$\overline{CV}_2$ - Pooled Coefficient of Variation based on the data for the 18 generated samples.

$\overline{CV}_S$ - Coefficient of Variation of the sample collection, the value is dependent on the data from the 18 analytical and 18 generated samples.

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

$\overline{CV}_P$ - Coefficient of Variation due to the pump error, assumed to be equal to 0.05.

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

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

or:

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

Grubb's Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

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

where:

x = observation being tested

$\bar{x}$ = mean of all observations

s = standard deviation based on n degrees of freedom.

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

Bartlett's Test for Homogeneity of Coefficients of Variances

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

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

where:

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

$\overline{CV}_{2i}$ = Coefficient of Variation of 6 generated samples at the i^{th} level.

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

i = 1, 2, 3..... n

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

k = number of variances being tested; in this program k = 3.

In order to pass Bartlett's test at the 1% significance level, chi squared must be less than or equal to 9.21 when k = 3.

Reference

A. Kenneth A. Busch Memoranda to Deputy Director, DLCD, on the subject "Statistical Protocol for Analysis of Data from Contract No. CDC-99-74-45", dated 1/16/75, 11/8/74.

Iron Oxide Fume

Analyte:	Iron Oxide Fume	Method No.:	S366
Matrix:	Air	Range:	3.9-18.2 mg/cu m
OSHA Standard:	10 mg/cu m	Precision ($\overline{CV}_T$):	0.067
Procedure:	Filter collection, atomic absorption	Validation Date:	11/26/76

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose ester membrane filter to collect iron oxide fume.

   1.2 The samples are ashed using hydrochloric and nitric acids to destroy the filter and other organic materials in the sample, and the iron oxide is then solubilized in nitric acid.

   1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for iron is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 3.87-18.19 mg/cu m using a 145-liter sample at an atmospheric temperature of 23°C and an atmospheric pressure of 764 mm Hg. Under the conditions of sample size (145 liters), the working range of the method is estimated to be 1.3-35.7 mg/cu m.

   2.2 The sensitivity of the sampling and analytical method for a 145-liter air sample using the 250-ml final solution volume is 143 micrograms of iron oxide, corresponding to 0.6 microgram/ml iron oxide. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling time, or by scale expansion to increase instrumental response.

3. Interferences

   3.1 Iron and other iron compounds which are collected on the cellulose ester membrane filter will cause a positive interference. The suspected identities of these compounds should be recorded and transmitted with the samples.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.87-18.19 mg/cu m is 0.067. This value corresponds to a 0.70 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.3. Details of the test procedures can be found in Reference 11.4.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no apparent bias in the sampling and analytical method. 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

The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter, 0.8-micrometer pore size mixed cellulose ester membrane filter, and an appropriate 37-mm three-piece cassette filter holder.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.3 Atomic absorption spectrophotometer equipped with an air-acetylene burner head.

6.3.1 Iron hollow cathode lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure-reducing valves: A 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank.

6.4 Manometer.

6.5 Thermometer.

6.6 Glassware, borosilicate

6.6.1 Phillips beakers: 100-ml.

6.6.2 Watchglass covers.

6.6.3 Pipets, delivery or graduated: 1, 3, 5, 7, and 10-ml.

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6.6.4 Volumetric flasks: 250-ml.

6.7 Polyethylene Bottles

6.7.1 Five 100-ml capacity polyethylene bottles for working atomic absorption standards.

6.7.2 One 1000-ml capacity polyethylene bottle for stock atomic absorption standard.

6.8 Hot Plate: Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, concentrated.

7.3 Nitric acid, dilute: 5 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water.

7.4 Hydrochloric acid, 1:1 solution in distilled water.

7.5 Iron metal for preparation of AA standards.

7.6 Iron oxide powder, Fe_2O_3, 325 mesh.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 cassette 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. Secure the cassette holder together with tape or shrinkable band.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

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

8.3.4 A sample size of 150 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%.

8.3.5 Since the filter may become plugged by oil mist or overloaded as evidenced by caking, the filter and pump's sampling rate should be checked periodically. When the filter becomes overloaded or when the pump's flow rate cannot be adjusted to 1.5 liters per minute, terminate sampling.

8.3.6 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.

8.3.7 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples, except that no air is drawn through it. Label this as a blank.

8.3.8 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 100-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample with 3 ml of 1:1 hydrochloric acid to solubilize any iron oxide which may be present. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Repeat twice. Repeat this procedure again three times except use concentrated nitric acid instead of hydrochloric acid. After the digestion process is complete, cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a fume hood until a white ash appears. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse the sides of the beaker, and allow to evaporate to dryness.

8.4.3 Cool each beaker and dissolve residues in 12.5 ml concentrated nitric acid.

8.4.4 Quantitatively transfer the clear solutions to a 250-ml volumetric flask.

8.4.5 Rinse each beaker at least three times with 2-3 ml portions of distilled or deionized water and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 250 ml with distilled or deionized water.

8.4.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 248.3 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume before aspiration. In such a case, use no more acid solution in 8.4.3 than is necessary to effect a quantitative transfer.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

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 iron oxide. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Place one 0.8-micron cellulose ester membrane filter into each of 24 clean 100-ml beakers. Amounts of iron oxide powder (Fe_2O_3) (to the nearest 0.01 mg) equal to the amount collected in a 150-liter sample at 2X, 1X, and 0.5X the OSHA standard level are added to the beakers: six at each level and six blanks. Three milligrams is the amount of Fe_2O_3 used at the 2X level; 1.5 mg at the 1X level; and 0.75 mg at the 0.5X level. The filters are then analyzed according to the method in Section 8.4.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or,

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

9.1 Prepare a 100 microgram/ml iron stock standard by dissolving 0.100 g iron metal in 50 ml hot concentrated nitric acid and diluting to 1 liter. Transfer to a 1-liter polyethylene bottle.

9.2 From the 100 ppm stock standard, prepare at least five working standards to cover the range from 250 to 2500 micrograms/250 ml. Prepare all standard solutions in dilute nitric acid and remake each day. Store the standard solutions in 100-ml polyethylene bottles.

9.3 Aspirate each of the standard samples and record the absorptions.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/250 ml.

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

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

where:

$$\text{microgram sample} = \text{microgram found in sample filter}$$

$$\text{microgram blank} = \text{microgram found in blank filter}$$

10.3 Corrections for analytical method recovery (A.M.R.) must be made.

$$\text{Corrected microgram/sample} = \frac{\text{microgram (Section 10.2)}}{\text{A.M.R.}}$$

10.4 Calculate the micrograms of iron oxide by multiplying the micrograms iron found (Section 10.3) by 1.43, which is a conversion factor to convert micrograms iron to micrograms iron oxide.

10.5 For personal sampling pumps with rotameters only, the following air 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)

10.6 The concentration of iron oxide in the air sample can be expressed in mg/cu m (microgram/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{microgram (Section 10.4)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

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

11.4 Backup Data Report for Iron Oxide Fume, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S366

Substance

Iron Oxide Fume

Standard

8-hour time-weighted average: 10 mg/cu m

Analytical Method

A known volume of air is drawn through a cellulose ester membrane filter to trap the iron oxide present. The filter is digested with nitric and hydrochloric acids to destroy the filter and any other organic material. The iron oxide is then solubilized in nitric acid and aspirated into an atomic absorption spectrophotometer for determination of concentration. The method has been validated over the range of 3.87-18.19 mg/cu m using a 145-liter sample at 23°C and 764 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at approximately 1.5 liters per minute; a 37-mm three piece cassette filter holder and a 37-mm/0.8-micrometer mixed cellulose ester membrane filter (MCEF) supported by a cellulose backup pad.

Sample Size

A sample size of 150 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

Sampling Procedure

1. Assemble the filter and three-piece filter cassette and close firmly to insure that the center ring seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

2. Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3. Air being sampled should not be passed 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 that is used.

5. Since the filter may become plugged by oil mist or overloaded as evidenced by caking, the filter and pump's sampling rate should be checked periodically. When the filter becomes overloaded or when the pump's flow rate cannot be adjusted to 1.5 liters per minute, terminate sampling.

6. After termination of sample collection, the cassettes should be firmly sealed with the plugs in both the inlet and outlet.

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

8. With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

Special Consideration

Because other iron compounds will be a positive interference, the presence of other iron compounds and their suspected identities should be recorded and transmitted with the samples.

Shipping Instructions

The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

Reference

Iron Oxide Fume, NIOSH Method No. S366.

Backup Data Report

Substance:	Iron Oxide Fume, No. S366
OSHA Standard:	10 mg/cu m
Chemicals Used for Validation:	Fe_3O_4 (Matheson, Coleman, and Bell), Fe_2O_3 (Alfa Ventron), and Ferric Citrate (J. T. Baker)

General

The procedure for collection and analysis of air samples of iron oxide fume is described in NIOSH Method No. S366. This method consists of collection of iron oxide on mixed cellulose ester membrane filters (MCEF), wet ashing the filters with hydrochloric and nitric acids, dissolving the iron oxide with nitric acid, and analysis of the resulting solutions by atomic absorption.

This method has been validated for a 145-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 iron oxide to represent 150-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 collection efficiency of the MCE filters.

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. S366. The results of the analytical method recovery tests are in Table S366-6 of this report.

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The definition of iron oxide fume was not clear from the documentation (Reference 2), so a decision was made jointly between NIOSH and the contractor to base the study on Fe_2O_3. However, to ensure that Fe_3O_4 would also be measured, a synthetic sample composed of Fe_3O_4 was studied by the analytical method described for iron oxide fume, Method S366. The results are presented below:

Table S366-1

Micrograms Fe_3O_4	Micrograms Fe taken	Micrograms Fe found	A.M.R.
3000	2171	2117	0.975
3210	2323	2193	0.944
3220	2300	2240	0.974
3175	2297	2129	0.927
3275	2370	2256	0.952
3210	2323	2198	0.946
		mean	0.953
		std dev	0.019
		CV_1	0.020

Recoveries were adequate so the method is suitable for mixed iron oxides. However, the method gives results only in terms of the iron content which could be considered a serious shortcoming.

Sampling and Analysis

Samples of iron oxide particulate were generated by thermal decomposition and oxidation of a ferric citrate aerosol. An Environmental Research Corporation fluid atomization aerosol generator was used to generate ferric citrate aerosol from a solution containing 10 g of ferric citrate dissolved in water and made up to 100 ml. Oxygen was used to generate the aerosol to assure complete oxidation of the citrate upon its decomposition.

The ferric citrate aerosol/O_2 output from the generator entered a 24-in long x 1-in I.D. quartz tube. The initial 12 inches of the tube was heated with a tube furnace to approximately 1100°C. The final 12 inches was wrapped in heating tape. The temperature of the gases (at a flow rate of 10.64 liters/minute) leaving the quartz tube was approximately 450°C. (See Figure S366-1)

The average residence time of particles in the furnace, at temperatures of at least 450°C, was 1.7 second. This is ample time to allow decomposition of the ferric citrate and its complete oxidation to iron oxide. This was verified by several experiments. Samples of the generated material were submitted for index of refraction and X-ray diffraction analyses. Both procedures quantitatively showed the material present to contain Fe_2O_3. Optical and electron microscopy showed the particles to have an acceptable size range. Scanning electron micrographs showed a size range of 0.24 to 1.39 microns.

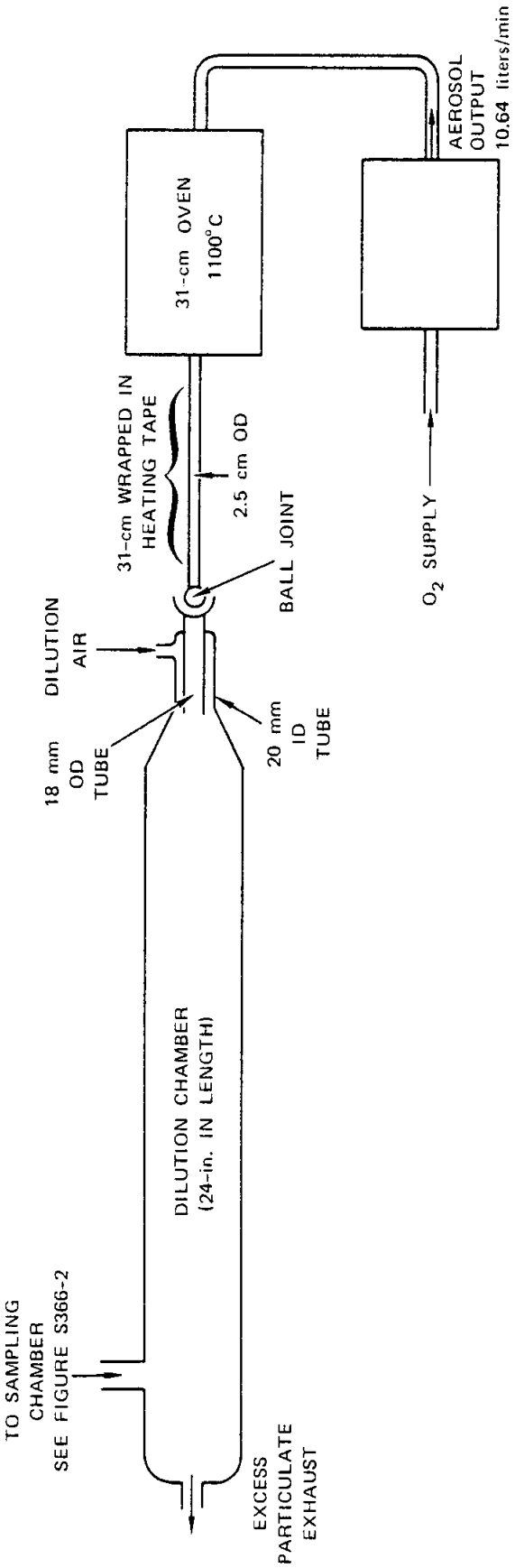

FIGURE S366-1

The concentration in the generator was monitored within the range of the instrument but without a high degree of reproducibility using a Thermo-Systems Model 3200 Particle Mass Monitor. This monitoring method was not considered to be accurate enough for determining "taken" concentrations. It was useful, however, for preliminary experiments in establishing a concentration range.

The output of the fluid atomization aerosol generator was held constant at 10.64 liters/minute while the dilution air flow rate was changed to achieve the desired concentration levels. Dilution air at a rate of 56 liters/minute was used for the generation of the 2X OSHA standard level; for the 1X OSHA level, a flow rate of 112 liters/minute was used and for the 0.5X OSHA level, 224 liters/minute of dilution air was used. Samples were collected for 100 minutes at an average flow rate of 1.485 liter/minute.

The iron oxide particles enter a dilution chamber through a 18-mm O.D. glass tube which is concentric with a 20-mm I.D. glass tube which delivers the dilution air. Air enters a 70-cm dilution chamber by a 54-mm O.D. dilution tube at a high velocity where turbulent mixing of the dilution air and aerosol takes place.

As shown in Figure S366-1, iron oxide particles in the dilution chamber are pulled into the sampling cone (Figure S366-2) at a rate of approximately 13 liters/minute which is controlled by a 0.052-in critical orifice under a 25-in Hg vacuum. Thus, it is necessary to have a total air flow of at least 13 liters/minute in the dilution chamber.

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

The results of the Sampling and Analysis experiments are presented in Table S366-7.

Collection Efficiency

Collection efficiency tests were conducted at 18.19 mg/cu m (as determined by analysis of samples collected at 2X the OSHA standard level) by mounting in series two filters in direct contact with each other. The results of the collection efficiency test are given below:

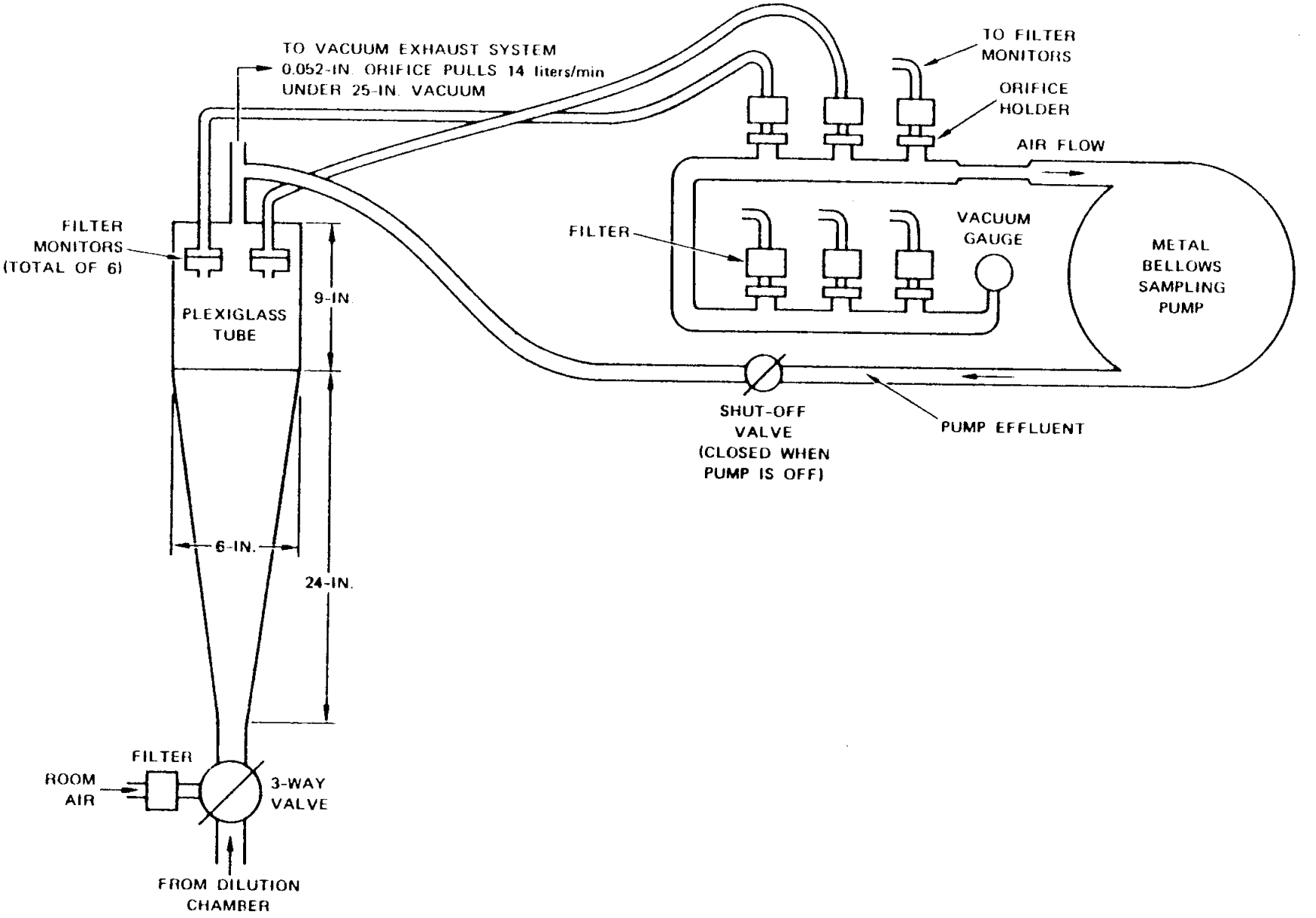

Figure S366-2 SAMPLING CHAMBER

S366-5

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Table S366-2

	mg/cu m found first filter	mg/cu m found backup filter	Collection Efficiency
	18.61	N.D.*	1.00
	18.87	N.D.*	1.00
	17.91	N.D.*	1.00
	18.74	N.D.*	1.00
	17.64	N.D.*	1.00
	17.38	N.D.*	1.00
mean	18.19		

*N.D. = Not detected at a detection limit of 0.03 mg/cu m.

Since collection efficiency was determined to be 1.00 on MCE filters, no correction for collection is needed.

Storage Stability Study

A study was done to assess whether iron oxide would be successfully stored for one week after collection. A second set of six samples at the 1X OSHA standard level was collected. It was not possible to collect the time study samples simultaneously with the samples used in the validation study using the apparatus previously described in the Generation Section. Therefore, it was necessary to determine the constancy of the generator over a long period of time. Fluctuations in the generator output between collection of the two sets of samples would place a bias on the time study recovery results. To establish the performance of the generator system, two samples were collected in each of three 100-minute sampling periods. Comparison of the sample concentrations of the three generations varied by 1.7% during the 5-hour period. Thus, it is likely that no significant bias was introduced.

The results of the storage stability study are given below:

Table S366-3

	Sample Analyzed Immediately (mg/cu m)	Samples Analyzed After One Week (mg/cu m)
	10.99	11.10
	11.27	11.01
	11.33	11.33
	10.21	10.12
	11.66	11.50
	11.15	11.04
mean	11.10	11.02
std dev	0.49	0.48
CV	0.044	0.044

The criterion for acceptance was that the mean of the six samples stored at room temperature for 7 days should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The mean of the samples taken at the beginning of the storage period was 11.10 mg/cu m (see Table S366-7). The two means compare within 1%; thus, the storage stability was adequate.

Discussion

Two sets of samples were generated that were not used in the validation study, because the levels were not acceptable. The same generation parameters described under the Sampling and Analysis section for the 0.5X level were used. The results of the analysis of these samples are presented in Table S366-4. (An analytical method recovery of 0.968 was used to calculate corr. micrograms of iron.)

Table S366-4

Micrograms Fe	Corr. Micrograms Fe	Micrograms Fe_2O_3	Liters	mg/cu m
659	681	973	143.7	6.77
706	729	1042	149.0	6.99
566	585	837	136.1	6.15
628	649	928	145.5	6.38
690	713	1020	147.2	6.93
659	681	974	143.7	6.78
			mean	6.67
			std dev	0.33
			CV	0.049
97	103	147	149.4	0.98
97	103	147	149.4	0.98
95	98	140	149.6	0.94
95	98	140	141.0	0.99
104	107	153	153.6	1.00
Sample discarded because of leakage.				
			mean	0.98*
			std dev	0.02
			CV	0.02

*The impactor plate from the cyclone was not removed during generation of these samples which may account for these low values.

Independent Method

The concentration of iron oxide fume in the generator was determined by collecting two additional samples on 47-mm MCE filters placed in open faced cassettes. This was done only at 0.5X the OSHA standard level. These samples were collected at a flow rate of approximately 2.5 liters per minute for 100 minutes. The results of the analysis of these samples are presented in Table S366-5. (An analytical method recovery of 0.968 was used to calculate corr. micrograms of iron.)

Table S366-5

Micrograms Fe	Corr. Micrograms Fe	Micrograms Fe_2O_3	Liters	mg/cu m
603	623	891	248	3.59
644	665	920	250	3.68
			mean	3.64

Precision and Accuracy

The statistical procedures and a definition of the terms used are desdribed in Reference 3. A summary is given in Attachment A.

The precision of the analytical method was assessed using the data in Table S366-6. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.054.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S366-7 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 0.039.

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 0.067.

Table S366-6

Data Sheet: Iron Oxide Fume

Analysis

Level	Micrograms Fe_2O_3 taken	Micrograms Fe taken	Micrograms Fe found	A.M.R.
0.5X	808	566	540	0.954
	724	507	495	0.976
	798	559	592	1.059
	759	531	510	0.961
	848	594	570	0.960
	798	559	520	0.930
			mean	0.973
			std dev	0.045
			CV_1	0.046
1X	1532	1072	1080	1.008
	1582	1107	1147	1.036
	1500	1050	1036	0.987
	1851	1296	1103	0.851
	1517	1062	1000	0.942
	1432	1002	989	0.987
			mean	0.969
			std dev	0.063
			CV_1	0.067
2X	3284	2297	2205	0.960
	2934	2052	2136	1.041
	2956	2067	1927	0.932
	2768	1936	1826	0.943
	2999	2098	1928	0.919
	2829	1979	1922	0.971
			mean	0.961
			std dev	0.043
			CV_1	0.045

$\overline{CV}_1$ 0.054

$\overline{CV}_{A+\overline{AMR}}$ 0.058

An average analytical method recovery (A.M.R.) of 0.968 was used to calculate corr. micrograms in Tables S366-4, S366-5, and S366-7.

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Table S366-7

Data Sheet: Iron Oxide Fume

Sampling and Analysis

Test Level	Found: µg Fe	Corr. µg Fe	µg Fe_2O_3	Liters	mg/cu m*	Taken: mg/cu m	Percent Recovery
0.5X	397	410	586	149.4	3.92	3.64	
	391	404	578	149.4	3.87	3.64	
	404	417	596	149.6	3.98	3.64	
	405	418	598	150.6	3.97	3.64	
	372	384	549	141.0	3.89	3.64	
	376	388	555	153.6	3.61	3.64	
				n = 6			
				mean	3.87		
				std dev	0.14		
				CV_2	0.036		106.3
1X	1069	1104	1579	143.7	10.99		
	1136	1174	1679	149.0	11.27		
	1043	1078	1542	136.1	11.33		
	1006	1039	1486	145.5	10.21		
	1162	1200	1716	147.2	11.66		
	1084	1120	1602	143.7	11.15		
				n = 6			
				mean	11.10		
				std dev	0.49		
				CV_2	0.044		
2X	1810	1870	2674	143.7	18.61		
	1903	1966	2811	149.0	18.87		
	1649	1704	2437	136.1	17.91		
	1846	1907	2727	145.5	18.74		
	1758	1816	2597	147.2	17.64		
	1691	1747	2498	143.7	17.38		
				n = 6			
				mean	18.19		
$\overline{CV_2}$ 0.039				std dev	0.63		
				CV_2	0.035		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

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 the Threshold Limit Values for Substances in Workroom Air, Third Ed., (1971).

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

4. Friedman and Horstman, "Method for Generation of Metallic Oxide Aerosols," Amer. Ind. Hyg. Assoc. J., 35, 12, (1974), 825-831.

Attachment A

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 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.

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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.

Methylcyclohexanone*

Analyte:	Methylcyclohexanone	Method No.:	S375
Matrix:	Air	Range:	210-850 mg/cu m
OSHA Standard:	100 ppm (460 mg/cu m) - skin	Precision ($\overline{CV}_T$):	0.057
Procedure:	Adsorption on Porapak Q, desorption with acetone, GC	Validation Date:	2/18/77

1. Principle of the Method

1.1 A known volume of air is drawn through a glass tube containing Porapak Q to trap methylcyclohexanone vapors.

1.2 Methylcyclohexanone is desorbed from the Porapak Q with acetone, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

2.1 This method was validated over the range of 213-852 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 759 mm Hg, using a 3-liter sample. This maximum sample size is based on the capacity of the Porapak Q to collect vapors of methylcyclohexanone 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 Porapak Q. This capacity may vary with the concentrations of methylcyclohexanone and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for three hours at an average sampling rate of 0.044 liter/minute and relative humidity of greater than 80% and temperature of 23°C. The breakthrough test was conducted at a concentration of 852 mg/cu m.

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* Methylcyclohexanone is a mixture of isomers, primarily 3-methylcyclohexanone and 4-methylcyclohexanone.

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 methylcyclohexanone 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 213-852 mg/cu m was 0.057. This value corresponds to a 26 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% higher than the "true" concentrations for 17 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 426 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 methylcyclohexanone found on the backup section of the Porapak Q 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 Porapak Q Tubes: Glass tube with both ends unsealed, 8.5-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 50/80 mesh Porapak Q* separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Porapak Q, and the backup section contains 75 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 0.05 liter per minute. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. The Porapak Q tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to useage, Porapak Q is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch to batch differences in production. A quantitity of Porapak Q is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Porapak Q, 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 (4-ft long x 1/8-in O.D. stainless steel) packed with 50/80 mesh Porapak Q.

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 Polyseal** caps or equivalent.

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.

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* Porapak Q is a solid adsorbent which is manufactured by Waters Associates, Inc., and is commonly used as a gas chromatographic column packing material.

**The Polyseal Corp., Baltimore, Md.

6.11 Manometer.

7. Reagents

7.1 Acetone, reagent grade.

7.2 3-Methylcyclohexanone, quantitative grade from Polyscience Corp., or equivalent.

7.3 4-Methylcyclohexanone, quantitative grade from Polyscience Corp., or equivalent.

7.4 n-Hexane, chromatographic quality.

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 Porapak Q tube in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.3)

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of Porapak Q 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 Porapak Q.

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

8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 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 Porapak Q 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.

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 Polyseal cap or equivalent. This sample should not be transported in the same container as the Porapak Q tubes. A minimum of 18 extra Porapak Q tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Porapak Q tube. Remove the glass wool plug and transfer the first (larger) section of Porapak Q to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Porapak Q to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to affect complete transfer of the Porapak Q.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the methylcyclohexanone 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
65 ml/min (24 psig) hydrogen gas flow to detector
500 ml/min (50 psig) air flow to detector
200°C injector manifold temperature
260°C detector manifold temperature
190°C column temperature

A retention time of approximately 9 minutes is to be expected for methylcyclohexanone under these conditions and using the column recommended in Section 6.4. The acetone will elute from the column before the methylcyclohexanone. A single peak will be observed for the isomers.

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 Porapak Q.

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 Porapak Q 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 Porapak Q.

8.5.2 Porapak Q equivalent to the amount in the first section of the sampling tube (150 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This Porapak Q must be from the same batch as that used in obtaining the samples. The open end is capped with Parafilm. A known amount of a hexane solution of a 50/50 mixture of 3-methylcyclohexanone and 4-methylcyclohexanone containing 345 mg/ml is injected directly into the Porapak Q with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 3-liter air sample at the

selected level. It is not practical to inject the neat liquid directly onto the Porapak Q, because the amounts to be added would be too small to measure accurately.

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 assure complete adsorption of the methylcyclohexanone onto the Porapak Q. 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 methylcyclohexanone into 1.0 ml of acetone 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 mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of methylcyclohexanone collected on the Porapak Q. Plot the desorption efficiency versus weight of methylcyclohexanone 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 mg/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 a stock standard solution containing 41.4 mg/ml of a 50/50 mixture of 3-methylcyclohexanone and 4-methylcyclohexanone in acetone.

9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in acetone. Prepare at least 5 working standards to cover the range of 0.138-4.14 mg/1.0 ml. This range is based on a 3-liter sample.

9.3 Prepare a standard calibration curve by plotting concentration of methylcyclohexanone in mg/1.0 ml versus peak area.

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/1.0 ml acetone 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.

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg 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 mg/sample.

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

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 methylcyclohexanone in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 o-methylcyclohexanone
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

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

11.2 Backup Data Report for Methylcyclohexanone, 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. S375

Substance

Methylcyclohexanone*

Standard

8-hour time-weighted average: 100 ppm (460 mg/cu m) - skin

Analytical Method

A known volume of air is drawn through a tube containing 50/80 mesh Porapak Q to trap the methylcyclohexanone vapors present. The methylcyclohexanone is desorbed from the Porapak Q with acetone 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 213-852 mg/cu m for a 3-liter sample at 22°C and 759 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 0.05 liter per minute. A tube (8.5-cm long with a 6-mm O.D. and a 4-mm I.D.), containing two sections of 50/80 mesh Porapak Q separated by a 2-mm portion of urethane foam, is used to collect the samples. The front section of the tube contains 150 mg of Porapak Q, and the back section contains 75 mg. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. Prior to packing, Porapak Q is prewashed in acetone.

Sample Size

A maximum sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. Do not sample at a flow rate less than 0.01 liter per minute.

Sampling Procedure

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

* Methylcyclohexanone is a mixture of isomers of methylcyclohexanone, primarily 3-methylcyclohexanone and 4-methylcyclohexanone.

2. The smaller section of Porapak Q 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 Porapak Q tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of methylcyclohexanone.

3. Air being sampled should not be passed through any hose or tubing before entering the Porapak Q 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 Porapak Q 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. With each batch of ten samples, submit one Porapak Q 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. Label this tube as a blank. Information on the batch number of the Porapak Q must be supplied. A minimum of 18 extra Porapak Q tubes should be provided for desorption efficiency determinations.

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 Porapak Q 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 Polyseal* cap or equivalent. Label of the bulk sample should match air samples for identification purposes.

*The Polyseal Corp., Baltimore, MD.

Shipping Instructions

Capped Porapak Q 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

Methylcyclohexanone, NIOSH Method No. S375.

Backup Data Report No. S375

Substance:	Methylcyclohexanone*
OSHA Standard:	100 ppm (460 mg/cu m) - skin
Chemical Used for Validation:	50/50 Mixture of 3-methylcyclohexanone and 4-methylcyclohexanone from Polyscience Corp., Niles, Ill.

General

The procedure for collection and analysis of air samples of methylcyclohexanone is described in NIOSH Method No. S375. This method consists of collection of the sample on Porapak Q, desorption with acetone, and analysis of the resulting solution by gas chromatography.

This method has been tested for validity for a 3-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 methylcyclohexanone to represent 3-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 Porapak Q 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. S375. The results of the desorption efficiency tests are in Table S375-15 of this report. Porapak Q, Lot 1271, was used in the validation study.

* Methylcyclohexanone is a mixture of isomers of methylcyclohexanone, primarily 3-methylcyclohexanone and 4-methylcyclohexanone.

Sampling and Analysis

Test atmospheres of methylcyclohexanone in air were generated with a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-ml syringe was filled with the analyte and placed in the syringe drive pump. A 15-inch long stainless steel needle was attached to the syringe. The needle passed through a rubber septum which enters into a heated glass tube. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen. It was diluted with air immediately downstream from the heated zone to obtain 2X the OSHA standard level. Dilutions to 1X and 0.5X the OSHA standard level were made as described in Attachment A. A total hydrocarbon analyzer was used to monitor the stability of the concentration of the analyte in each of the three test chambers. The samples were collected as described in Method S375 using sampling tubes packed with 50/80 mesh Porapak Q.

Six samples were collected for 4000 seconds from each chamber to obtain 3-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 S375-16 of this report. 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 90 micrograms/milliliter.

Storage Stability Study

A study was done to assess whether methylcyclohexanone 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. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results of the analyses are given below:

Table S375-1: Storage Stability

Samples Analyzed Immediately (mg/cu m)	Samples Analyzed After 7 Days (mg/cu m)
418	413
422	429
406	431
426	447
389	422
415	446
mean 413	431
std dev 13	13
CV 0.031	0.030

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 mean of the

samples taken at the beginning of the storage period was 413 mg/cu m (see Table S375-16). The two means compare within 4%; thus, the storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed at a relative humidity of greater than 80%. Details of the method of generating atmosphere containing high relative humidities are given in Attachment B.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) 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.

The breakthrough time was measured by testing in parallel 6 sampling tubes, each containing 150 mg of Porapak Q. The tubes were placed in the sample generation apparatus. The test atmosphere was caused to flow through each tube at the flow rates to be used during sample collection. Sampling flow rates were regulated with the use of 0.003-inch orifices for a rate of 0.044 liter per minute. The orifices were connected to a manifold, which was evacuated to about 22 inches of Hg using a metal bellows pump. This pump was selected, because it does not leak and is constructed entirely of stainless steel; therefore, it will not alter the composition of the test atmosphere.

For the breakthrough tests, the effluent from the pump was monitored with a gas chromatograph with a 2-ml sampling loop. The response of the gas chromatograph to the pump effluent was compared with the response for the atmosphere being sampled. Peak area measurements were used to determine the concentration of methylcyclohexanone in the pump effluent, and these areas were compared with peak areas when the test chamber was sampled.

Breakthrough did not occur when the average sampling rate was 0.044 liter per minute when the relative humidity was greater than 80%. The concentration tested was 852 mg/cu m. Sampling was discontinued after 185 minutes. The breakthrough test was discontinued after 185 minutes, because the supply of analyte was depleted.

Discussion

Work on methylcyclohexanone was initially performed with charcoal lots 104 and 105 and silica gel. Recoveries of methylcyclohexanone from charcoal decreased severely after seven days. Satisfactory recoveries (D.E.'s) were obtained on silica gel, however, silica gel did not have sufficient capacity to adsorb methylcyclohexanone at high relative humidity. The results of the recovery of methylcyclohexanone on charcoal and on silica gel are presented below. Note: The sample size used

for charcoal was 12 liters, but the sample size was decreased to 3 liters on silica gel.

Table S375-2: Desorption Efficiency, Charcoal Lot 105

Desorption efficiency from Charcoal Lot 105 (100 mg) of a mixture of the 3 and 4 isomers of methylcyclohexanone assuming a 12-liter sample at 1X the OSHA standard. These samples were stored for one day and desorbed with 1 ml of CS_2.

mg taken	mg found	D.E.
5.52	4.50	0.815
5.52	4.53	0.821
5.52	4.31	0.781
5.52	4.10	0.743
5.52	4.36	0.790
5.52	4.18	0.757
	mean	0.784
	std dev	0.031
	CV	0.040

Table S375-3: Desorption Efficiency, Charcoal Lot 104

Desorption efficiency from Charcoal Lot 104 (100 mg) of a mixture of the 3 and 4 isomers of methylcyclohexanone assuming a 12-liter sample at 1X the OSHA standard. These samples were stored for one day and desorbed with 1 ml of CS_2.

mg taken	mg found	D.E.
5.52	5.07	0.918
5.52	5.20	0.942
5.52	4.85	0.879
5.52	4.70	0.851
5.52	4.73	0.857
5.52	4.45	0.806
	mean	0.876
	std dev	0.049
	CV	0.056

Table S375-4: Desorption Efficiency, Charcoal Lot 104

Desorption efficiency from Charcoal Lot 104 (100 mg) of 2-methylcyclohexanone assuming a 12-liter sample at 0.5X the OSHA standard. These samples were stored for one day and desorbed with 1 ml of CS_2.

mg taken	mg found	D.E.
2.76	2.55	0.924
2.76	2.46	0.891
2.76	2.41	0.873
2.76	2.58	0.935
2.76	2.48	0.899
	mean	0.904
	std dev	0.025
	CV	0.028

Table S375-5: Desorption Efficiency, Charcoal Lot 104

Desorption efficiency from Charcoal Lot 104 (100 mg) of 3-methylcyclohexanone assuming a 12-liter sample at 0.5X the OSHA standard. These samples were stored for three days and desorbed with 1 ml of CS_2.

mg taken	mg found	D.E.
2.76	2.37	0.859
2.76	2.27	0.822
2.76	2.08	0.754
2.76	2.08	0.754
2.76	2.04	0.739
2.76	2.05	0.743
	mean	0.778
	std dev	0.050
	CV	0.064

Table S375-6: Desorption Efficiency, Charcoal Lot 104

Desorption efficiency from Charcoal Lot 104 (100 mg) of 4-methylcyclohexanone assuming a 12-liter sample at 0.5X the OSHA standard. These samples were stored for 1 day and desorbed with 1 ml of CS_2.

mg taken	mg found	D.E.
2.76	2.37	0.859
2.76	2.43	0.880
2.76	2.29	0.830
2.76	2.40	0.870
2.76	2.50	0.906
2.76	2.56	0.928
	mean	0.879
	std dev	0.035
	CV	0.040

Table S375-7: Desorption Efficiency, Charcoal Lot 104

Desorption efficiency from Charcoal Lot 104 (100 mg) of 4-methylcyclohexanone assuming a 12-liter sample at 0.5X the OSHA standard. These samples were stored for 7 days and desorbed with 1 ml of CS_2.

mg taken	mg found	D.E.
2.76	1.70	0.616
2.76	1.66	0.601
2.76	1.67	0.605
2.76	1.61	0.583
2.76	1.55	0.562
2.76	1.55	0.562
	mean	0.588
	std dev	0.023
	CV	0.039

From the above results, it was shown that the recovery of the 3 and 4 isomers of methylcyclohexanone (Table S375-2) on charcoal Lot 105 was not satisfactory. Although the desorption efficiencies were satisfactory on charcoal Lot 104, the data in Table S375-7 indicate that methylcyclohexanone is not stable upon storage on charcoal for one week. It was therefore decided to test silica gel as a possible sorbent.

Table S375-8: Desorption Efficiency, Silica Gel

Desorption efficiency from silica gel (150 mg) of a mixture of the 3 and 4 isomers of methylcyclohexanone for a 3-liter sample at 0.5X the OSHA standard. These samples were stored for one day and desorbed with 1 ml of methanol.

mg taken	mg found	D.E.
0.690	0.652	0.945
0.690	0.708	1.026
0.690	0.681	0.987
0.690	0.696	1.009
0.690	0.690	1.000
0.690	0.690	1.000
	mean	0.994
	std dev	0.027
	CV	0.027

Table S375-9: Desorption Efficiency, Silica Gel

Desorption efficiency from silica gel (150 mg) of a mixture of the 3 and 4 isomers of methylcyclohexanone for a 3-liter sample at 1X the OSHA standard. These samples were stored for one day and desorbed with 1 ml of methanol.

mg taken	mg found	D.E.
1.380	1.377	0.998
1.380	1.416	1.026
1.380	1.353	0.980
1.380	1.368	0.991
1.380	1.383	1.002
1.380	1.368	0.991
	mean	0.998
	std dev	0.016
	CV	0.016

Table S375-10: Desorption Efficiency, Silica Gel

Desorption efficiency from silica gel (150 mg) of a mixture of the 3 and 4 isomers of methylcyclohexanone for a 3-liter sample at 2X the OSHA standard. These samples were stored for one day and desorbed with 1 ml of methanol.

mg taken	mg found	D.E.
2.760	2.720	0.986
2.760	2.724	0.987
2.760	2.707	0.981
2.760	2.707	0.981
2.760	2.654	0.962
2.760	2.676	0.970
	mean	0.978
	std dev	0.010
	CV	0.010

Table S375-11: Desorption Efficiency, Silica Gel

Desorption efficiency from silica gel (150 mg) of a mixture of the 3 and 4 isomers of methylcyclohexanone for a 3-liter sample at 1X the OSHA standard. These samples were stored for seven days and desorbed with 1 ml of methanol.

mg taken	mg found	D.E.
1.380	1.362	0.987
1.380	1.358	0.984
1.380	1.347	0.976
1.380	1.348	0.977
1.380	1.392	1.009
1.380	1.351	0.979
	mean	0.985
	std dev	0.012
	CV	0.012

The recoveries of methylcyclohexanone were satisfactory from silica gel. However, based on data for other similar substances, it was decided that silica gel would likely not have the capacity to adsorb methylcyclohexanone at high relative humidity. It was then decided to try Porapak Q as a possible sorbent.

Additional desorption efficiency experiments on the individual isomers of methylcyclohexanone on Porapak Q were performed. All of these samples were stored for one day and desorbed with 1 ml of acetone. The results are presented in Tables S375-12 to S375-14. These desorption efficiencies were found to be satisfactory and were compared to the desorption efficiencies in Table S375-15 which represents the desorption efficiencies for the mixture of the 3 and 4 isomers of methylcyclohexanone on Porapak Q. It was also found from the breakthrough study that Porapak Q has sufficient capacity to adsorb methylcyclohexanone at high relative humidity (see Breakthrough Section). It was therefore decided that Porapak would be used as the solid sorbent to collect the methylcyclohexanone.

Table S375-12: Desorption Efficiency, Porapak Q

Desorption efficiency from Porapak Q (150 mg) of 2-methylcyclohexanone for a 3-liter sample at 1X the OSHA standard level.

mg taken	mg found		D.E.
1.277	1.183		0.926
1.277	1.170		0.916
1.277	1.176		0.921
1.277	1.193		0.934
1.277	1.169		0.915
1.277	1.180		0.924
		mean	0.923
		std dev	0.007
		CV	0.008

Table S375-13: Desorption Efficiency, Porapak Q

Desorption efficiency from Porapak Q (150 mg) of 3-methylcyclohexanone for a 3-liter sample at 1X the OSHA standard level.

mg taken	mg found		D.E.
1.277	1.108		0.868
1.277	1.157		0.906
1.277	1.167		0.914
1.277	1.174		0.919
1.277	1.176		0.921
1.277	1.162		0.910
		mean	0.906
		std dev	0.020
		CV	0.022

Table S375-14: Desorption Efficiency, Porapak Q

Desorption efficiency from Porapak Q (150 mg) of 4-methylcyclohexanone for a 3-liter sample at 1X the OSHA standard level.

mg taken	mg found	D.E.
1.277	1.173	0.919
1.277	1.166	0.913
1.277	1.185	0.928
1.277	1.202	0.941
1.277	1.215	0.951
1.277	1.192	0.933
	mean	0.931
	std dev	0.014
	CV	0.015

Independent Method

The concentration of methylcyclohexanone in the generator was determined using the rate of delivery of the syringe drive and the flow rates of the dilution air. A total hydrocarbon analyzer was used to measure the constancy of the concentration of the analyte in the three test chambers. The following parameters were used to determine the "taken" concentration in the generator:

Syringe delivery:	30.89 mg/minute
Nitrogen flow rate:	4.48 liters/minute
Dilution air:	31.77 liters/minute

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2. A summary is given in Attachment C.

The precision of the analytical method was assessed using the data in Table S375-15. The pooled Coefficient of Variation (CV_1) for three sets of analytical samples was found to be 0.041.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S375-16 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 0.021. 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 101%. 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 0.057.

Table S375-15

Data Sheet: Methylcyclohexanone*

Analysis

Level**	0.5X		1X			2X		
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
0.732	0.673	0.919	1.464	1.388	0.948	2.928	2.639	0.901
0.732	0.650	0.888	1.464	1.400	0.956	2.928	2.419	0.826
0.732	0.711	0.971	1.464	1.351	0.923	2.928	2.765	0.944
0.732	0.678	0.926	1.464	1.378	0.941	2.928	2.780	0.949
0.732	0.681	0.930	1.464	1.372	0.937	2.928	2.715	0.927
0.732	0.702	0.959	1.464	1.344	0.918	2.928	2.901	0.991
n =		6			6			6
mean		0.932			0.937			0.923
std dev		0.030			0.015			0.056
CV_1		0.032			0.016			0.061

$\overline{CV_1}$ 0.041

$\overline{CV_{A+DE}}$ 0.044

An average desorption efficiency (D.E.) of 0.931 was used to calculate the corr. mg in Table S375-16.

* 50/50 mixture of the 3 and 4 isomers of methylcyclohexanone.

** The taken amounts represent 1.06 times the 0.5X, 1X, and 2X levels. These amounts were chosen for convenience in making up solutions.

Table S375-16

Data Sheet: Methylcyclohexanone*

Sampling and Analysis

Test Level	Found				Taken	Percent
	mg	Corr. mg	Liters	mg/cu m**	mg/cu m	Recovery
0.5X	0.625	0.671	3.05	220.0	213.0	
	0.636	0.683	3.00	227.7	213.0	
	0.648	0.696	3.03	229.7	213.0	
	0.630	0.677	2.98	227.2	213.0	
	0.649	0.697	3.02	230.8	213.0	
	Sample dropped as an outlier					
			n = 5			
			mean	227.1		106.6
			std dev	4.2		
			CV_2	0.018		
1X	1.159	1.245	2.98	418	426	
	1.187	1.275	3.02	422	426	
	1.172	1.259	3.10	406	426	
	1.219	1.309	3.07	426	426	
	0.956	1.027	2.64	389	426	
	1.153	1.238	2.98	415	426	
			n = 6			
			mean	413		96.9
			std dev	13		
			CV_2	0.031		
2X	2.454	2.636	3.09	853	852	
	2.270	2.438	2.90	841	852	
	2.232	2.397	2.86	838	852	
	2.393	2.570	3.04	845	852	
	2.128	2.286	2.67	856	852	
	2.449	2.630	3.07	857	852	
			n = 6			
			mean	848		99.5
			std dev	8		
$\overline{CV_2}$ 0.021			CV_2	0.009		

* 50/50 Mixture of the 3 and 4 isomers of methylcyclohexanone

** 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, NIOSH Contract CDC-99-74-45.

Attachment A

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 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

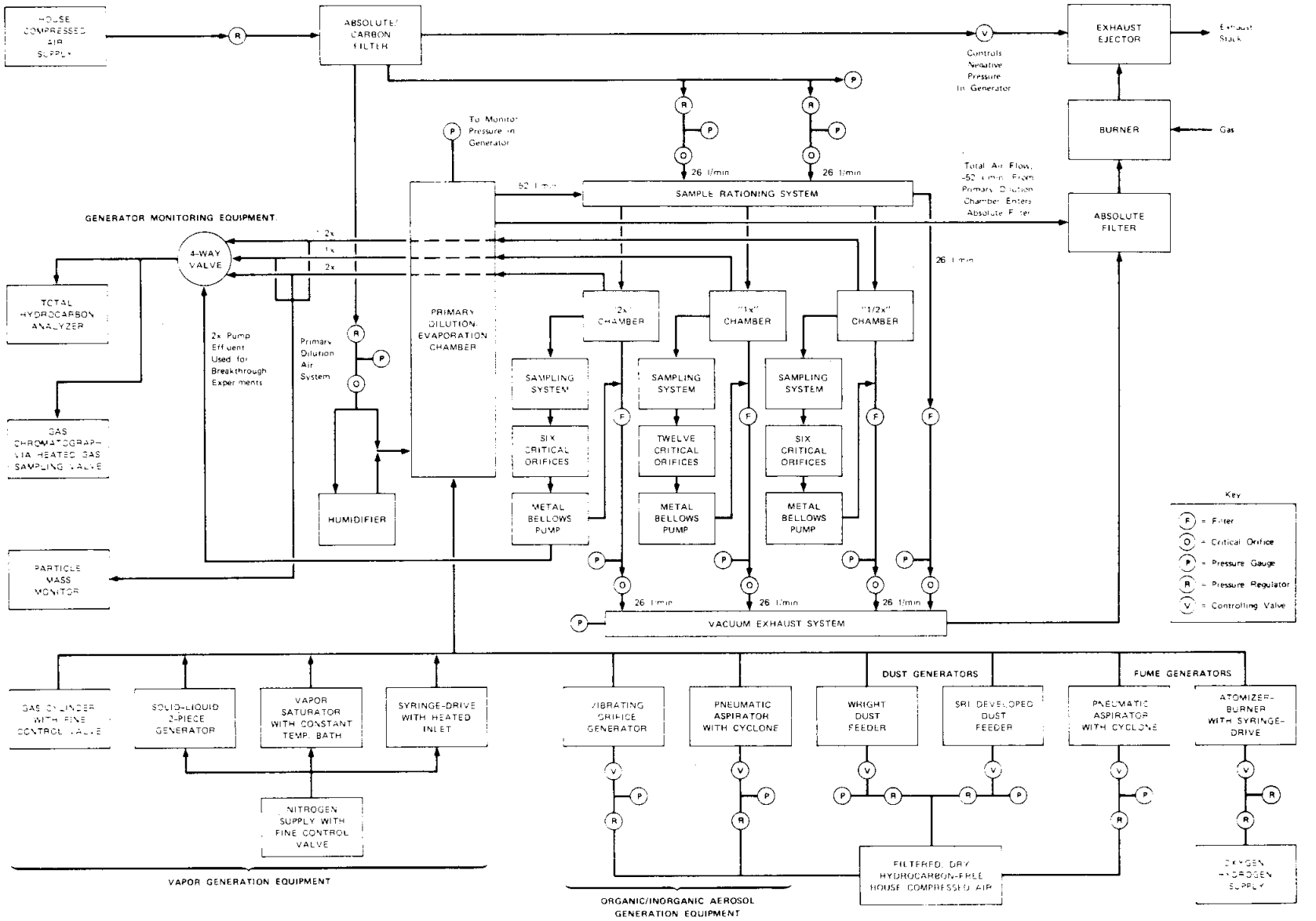


FIGURE S375-A1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

(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.

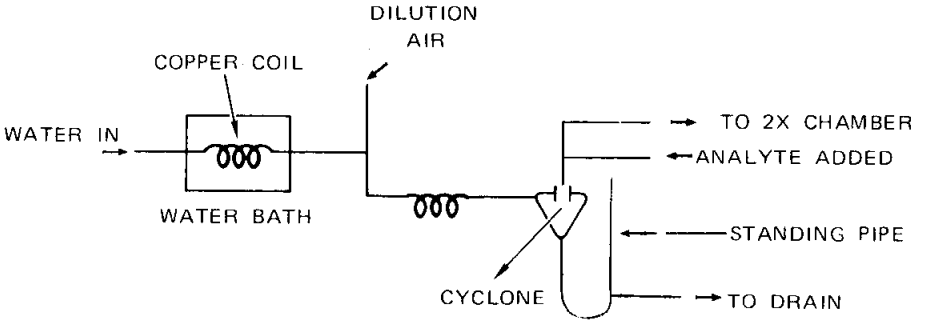
The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected 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 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 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.

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 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.

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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.

$$\overline{CV}_S = \sqrt{(\overline{CV}_2)^2 - (\overline{CV}_1)^1}$$

$\overline{CV}_P$ - 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.

Analyte:	Methyl Chloride	Method No.:	S99
Matrix:	Air	Range:	59-220 ppm (8-hr. T.W.A.) 143-580 ppm (Peak)
OSHA Standard:	100 ppm (8-hr. T.W.A.) 200 ppm (Ceiling) 300 ppm (Peak)	Precision (CV_T):	0.052
		Validation Date:	3/18/77
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC		

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through two tubes in series containing activated coconut charcoal to trap the gaseous methyl chloride.

   1.2 Methyl chloride is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 58.9-222 ppm for the time weighted average (T.W.A.) concentration and over the range of 143.4-582 ppm for the peak concentration. For the T.W.A. concentration, a sample size of 1.5 liters was collected. For the peak concentration, a sample size of 500 ml was collected. Both methods were validated at an atmospheric temperature of 25°C and atmospheric pressure of 760 mm Hg. The sample sizes used are based on the capacity of the charcoal to collect vapors of methyl chloride in air at a relative humidity of greater than 80%. 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 charcoal. This capacity may vary with the concentrations of methyl chloride and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 600 mg of charcoal) reaches 5% of the concentration in the test gas mixture. At a temperature of 22°C and relative humidity of 82%, breakthrough occurred in 135 minutes when a test concentration of 200 ppm was sampled at a flow rate of 0.0235 liter/minute. Breakthrough occurred in 24.4 minutes when a test concentration of 692 ppm at relative humidity of 84% was sampled at a flow rate of 0.105 liter/minute.

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 methyl chloride 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 (CV_T) for the total analytical and sampling method in the range of 58.9-222 ppm was 0.052. CV_T is based on the data for the T.W.A. concentrations. This value corresponds to a 5.2 ppm standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.

4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level for an 8-hour T.W.A. sample were 5.2% higher than the "true" concentrations for 17 samples. At the peak concentrations, the average concentrations obtained were 1% higher 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 318 ppm 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 uses a solid sorbent. 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 methyl chloride found on the backup charcoal tube exceeds 10% of that found in the front sections, 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 Charcoal Tubes: Two charcoal tubes are used in this method. One charcoal tube is used to collect the samples, and a smaller charcoal tube is used as a backup. The charcoal tubes are connected in series with Tygon tubing. The larger charcoal tube is a glass tube, approximately 10-cm long with a 8-mm O.D. and a 6-mm I.D. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal; the back section contains 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 0.05 liter per minute. The smaller charcoal tube is 7-cm long with a 6-mm O.D. and a 4-mm I.D. The smaller charcoal tube contains 100 mg of charcoal in the front section and 50 mg in the backup section.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 102.

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

6.6 Microliter Syringes: 10-microliter for injection of samples into the gas chromatograph.

6.7 Gas Tight Syringes: 0.1, 0.25, 0.50, and 1.0 ml sizes for preparing standards.

6.8 Pipets: 3.0-ml delivery pipets.

6.9 Serum Bottles: 15-ml glass bottles with 20-mm O.D. mouth.
Septa: 20-mm rubber septa with Teflon lining.
Aluminum tear-away seals to fit serum bottles.

6.10 Hand crimper for sealing septa to serum bottles.

6.11 Stopwatch.

6.12 Manometer.

7. Reagents

7.1 Methylene chloride, chromatographic quality, methyl chloride-free.

7.2 Methyl chloride, 99.5%.

7.3 Nitrogen, purified.

7.4 Hydrogen, prepurified.

7.5 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 charcoal tubes in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.4)

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.

8.3.2 Connect the larger charcoal tube in series with the smaller charcoal tube by connecting the backup section of the larger charcoal tube to the front section of the small charcoal tube with flexible vinyl tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearer the pump. Air should flow through the large charcoal tube before entering the small charcoal tube.

8.3.3 Both charcoal tubes should be vertical 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 charcoal tubes.

8.3.5 For peak concentration measurement, a sample size of 0.5 liter is recommended. Sample for 5 minutes at a flow rate of 0.10 liter per minute.

For T.W.A. concentration measurement, a sample size of 1.5 liters is recommended. Sample at a flow rate of 0.025 liter per minute.

Record sampling flow rates, collection time, and the 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 charcoal 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 large charcoal tube with the corresponding backup charcoal tube.

8.3.8 With each batch of ten samples, submit one set of tubes (a larger charcoal tube and a smaller backup tube) 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. A minimum of 18 charcoal tubes from the same batch of tubes should be provided for desorption efficiency tests during sample analysis.

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

8.4 Analysis of Samples

Upon receipt of the samples in the laboratory, the samples should be refrigerated if analysis cannot be done immediately.

8.4.1 Desorption of Methyl Chloride. Pipet 3.0 ml of methylene chloride into the 15-ml serum bottle. Remove the plastic caps from both ends of the larger charcoal tube. Remove the plug of urethane foam from the outlet end of the tube. Transfer the 200-mg portion of charcoal to the serum bottle. Next, remove the glass wool plug from the inlet end of the tube and transfer the 400-mg section of charcoal to the same bottle. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. It is important that the transfer of the charcoal be carried out as quickly as possible once the methylene chloride has been added to the bottle. The backup charcoal tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.

8.4.2 Gently shake the sample. The extract is now ready for analysis. Analyses should be completed within one day after the methyl chloride is desorbed. Prepare standards as in Section 8.5.3. Fresh standards should be prepared daily (throughout the day if possible).

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

40 ml/min (60 psig) nitrogen carrier gas flow rate
65 ml/min (24 psig) hydrogen gas flow rate to detector
500 ml/min (50 psig) air flow rate to detector
200°C injector temperature
260°C detector temperature
100°C column temperature

A retention time of approximately 3.0 minutes is to be expected for the analyte under these conditions and using the column recommended in Section 6.4. The methylene chloride will elute from the column after the methyl chloride.

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 microliter 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 for methyl chloride in methylene chloride.

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 charcoal 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 charcoal.

8.5.2 Known amounts of methyl chloride are sorbed from the gas phase on the charcoal in the tubes as described below:

The apparatus to be used for spiking charcoal with known amounts of methyl chloride consists of a union tee connected to a source of purified nitrogen, a charcoal tube, and a septum for introducing methyl chloride from a gas tight syringe. A known amount of methyl chloride is injected slowly through the septum where nitrogen at a flow rate of approximately 30 ml/min carries methyl chloride into the charcoal tube. The nitrogen is allowed to flow through the tube for an

additional 1 minute after discharge of the contents of the syringe through the septum. The charcoal tube is capped with plastic caps.

The amount sorbed is equivalent to that present in an air sample at the selected level and flow rate. This requires 0.075, 0.15, and 0.30 ml of methyl chloride for 0.5X, 1X, and 2X the OSHA T.W.A. and ceiling levels, respectively. The atmospheric temperature, pressure, and relative humidity at which the tubes are prepared should be recorded.

Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of methyl chloride onto the charcoal in the tube. 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.

8.5.3 Desorption and analysis experiments are done on the contents of the larger charcoal tube as described in Section 8.4.1.

In preparation of the standards, 3.0 ml of methylene chloride is added to a 15-ml serum bottle. The bottle is then sealed using a Teflon-lined septum and aluminum seal. An appropriate amount of methyl chloride gas is bubbled slowly into the methylene chloride, by means of a gas tight syringe.

The syringe needle should be immersed in the methylene chloride during discharge of methyl chloride from the syringe. The bottle should be shaken gently after removal of the syringe needle. Standards should be prepared at the same time that the sample analysis is done, and analyzed with the samples.

The weight (mg) of methyl chloride in each standard and sample is calculated by the formula in Section 9.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of methyl chloride collected on the charcoal. Plot the desorption efficiency versus weight of methyl chloride found. This curve is used to correct for losses, as described in Section 10.4.

9. Calibration and Standards

A series of standards, varying in concentration over the range of interest, is prepared as described in Section 8.5.3 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/3.0 ml versus peak area.

It is convenient to express concentration of standards in terms of mg/3.0 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The number of mg in the standard is calculated as follows:

$$mg = V \times \frac{M.W.}{24.45} \times \frac{298}{T + 273} \times \frac{P}{760}$$

where:

V	= ml of methyl chloride used to prepare the standard
T	= temperature (°C) at which the sample was prepared
P	= pressure (mm Hg) at which the sample was prepared
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight of methyl chloride (50.49 g/mole)
298	= standard temperature (°K)
760	= standard pressure (mm Hg)

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/3.0 ml methylene chloride 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. It may be necessary to run blanks on several lots of methylene chloride to determine which reagent is not contaminated with methyl chloride.

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

where:

mg sample = mg found in both sections of sample tube
mg blank = mg found in both sections of blank tube

A similar procedure is followed for the backup tubes.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the first tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

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

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 methyl chloride in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 methyl chloride
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

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

11.3 Backup Data Report for Methyl Chloride, prepared under NIOSH Contract No. 210-76-0123.

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

Sampling Data Sheet No. S99

Substance

Methyl Chloride

Standard

8-hour time-weighted average: 100 ppm
Ceiling: 200 ppm
Peak: 300 ppm (5 minutes in any 3 hours)

Analytical Method

A known volume of air is drawn through a tube containing activated coconut charcoal connected in series with a smaller backup charcoal tube to trap the methyl chloride vapors present. The methyl chloride is desorbed from the charcoal with methylene chloride, 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 58.9-222 ppm for the T.W.A. concentration and 143.4-582 ppm for the peak concentration at 25°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%). A charcoal tube, approximately 10-cm long with a 8-mm O.D. and a 6-mm I.D., containing two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam, is used to collect the samples. The front section of the tube contains 400 mg of charcoal, and the back section contains 200 mg. A smaller charcoal tube, 7-cm long with a 6-mm O.D. and a 4-mm I.D., is used as a backup tube. This second tube contains 100 mg of charcoal in the front section and 50 mg in the back section.

Sample Size

For measurement of the peak concentration, a sample size of 0.5 liter is recommended. Sample for 5 minutes at a flow rate of 0.10 liter per minute. For measurement of the T.W.A. concentration, a sample size of 1.5 liters is recommended. Sample at a flow rate of 0.025 liter/minute.

Sampling Procedure

1. Immediately before sampling, the ends of the large and small charcoal tubes should be broken so as to provide an opening at least one-half the internal diameter of the tube.

2. Connect the larger charcoal tube in line with the smaller charcoal tube by connecting the backup section of the larger charcoal tube to the front section of the small charcoal tube with flexible vinyl tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearer the sampling pump. Air should flow through the larger charcoal tube before entering the small charcoal tube. The charcoal tubes should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of methyl chloride.

3. Air being sampled should not pass through any hose or tubing before entering the charcoal 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 charcoal tubes should be separated and 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. Each set of tubes should be marked to identify the large charcoal tube with the corresponding backup charcoal tube.

6. With each batch of ten samples, submit one set of charcoal tubes (a larger charcoal tube and a smaller backup charcoal tube) 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. Label this set of tubes as a blank. Information on the batch number of the charcoal must be supplied. A minimum of 18 charcoal tubes from the same batch of tubes should be provided to the analyst for desorption efficiency tests during sample analysis.

Special Considerations

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.

2. Due to the high resistance of the sampling train, 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. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

Shipping Instructions

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

Reference

Methyl Chloride, NIOSH Method No. S99.

Backup Data Report No. S99

Substance:	Methyl Chloride
OSHA Standard:	8-hour Time weighted average: 100 ppm Ceiling: 200 ppm Peak: 300 ppm (5 minutes in any 3 hours)
Chemical Used for Validation:	Methyl Chloride, 99.5% Union Carbide

General

The procedure for collection and analysis of air samples of methyl chloride is described in NIOSH Method No. S99. This method consists of collection of the sample on activated coconut charcoal, desorption with methylene chloride, and analysis of the resulting solution by gas chromatography. Desorption efficiency experiments with carbon disulfide, ethanol, and chloroform gave poor results. Methylene chloride proved to be satisfactory.

This method has been tested for validity at the 8-hour T.W.A. and peak concentration levels, 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 methyl chloride to represent air samples at the 8-hour T.W.A. and peak concentration levels.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard) at the 8-hour T.W.A. and peak concentration levels.

Determine breakthrough capacity of activated coconut charcoal at high relative humidity for the 8-hour T.W.A. and peak concentration levels.

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. S99. The results of the desorption efficiency tests are in Table S99-4.

Sampling and Analysis

Test atmospheres of methyl chloride in air were generated in the system described in Attachment A. Samples were collected as described in Method S99 using two charcoal tubes connected in series. Methyl chloride gas was metered from the cylinder into this system. The gas was diluted with the appropriate amount of house air to obtain the desired 2X concentration. Dilutions to the 1X and 0.5X levels were made as described in Attachment A. A total hydrocarbon analyzer was used to monitor the constancy of the concentration in each sampling chamber. Separate experiments were made to generate test atmospheres at the T.W.A. and peak concentrations. Six samples were collected, each at 0.5X, 1X, and 2X the OSHA standard level, for each concentration. For the T.W.A. concentration, samples were collected for 65 minutes at an average flow rate of 0.024 liter/minute to obtain 1.5-liter samples. For the ceiling concentration, samples were collected for 5 minutes at an average flow rate of 0.105 liter/minute to obtain 0.5-liter samples. In addition, the backup tubes from samples collected at the 2X concentrations were analyzed and found to contain less than the limit of detection, which was 0.002 mg.

Storage Stability Study

A study was done to assess whether methyl chloride would be successfully stored for one week after collection. A second set of 6 samples at 1X the OSHA standard peak concentration was collected at the same time as the samples that were used for validation. These sample tubes were capped and stored on the laboratory bench for 7 days before analysis. The results of the analyses are given below:

Table S99-1

Samples Analyzed Immediately (ppm)	Samples Analyzed After Seven Days (ppm)
346	321
330	321
332	323
344	311
355	330
327	334
mean 339	323
std dev 11	8
CV 0.032	0.025

The criterion for acceptance was that the mean of the six samples stored at room temperature for 7 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

Two breakthrough tests were conducted. The T.W.A. breakthrough test was done at 82% relative humidity, and the breakthrough test for the peak concentration was done at 84% relative humidity. 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 600 mg of charcoal) 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 sample, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

The breakthrough time was measured by testing in paralled 6 sampling tubes, each containing 600 mg of activated coconut charcoal. The tubes were placed in the sample generation apparatus. The test atmosphere was caused to flow through each tube at the flow rates to be used during sample collection, using 0.002-inch and 0.0045-inch diameter orifices to regulate the flows. The orifices were connected to a manifold, which was evacuated to about 22 inches of Hg using a metal bellows pump. This pump was selected because it does not leak and is constructed entirely of stainless steel; therefore, it will not alter the composition of the test atmosphere.

For each breakthrough test, the effluent from the pump was monitored with a total hydrocarbon analyzer which was calibrated with bag standards. The response of the hydrocarbon analyzer to the effluent was compared to the response of the analyzer to the atmosphere being sampled. For the T.W.A. concentration, breakthrough occurred in 135 minutes when a test concentration of 200 ppm was sampled at a flow rate of 0.0235 liter/min. At the peak concentration, breakthrough occurred in 24.4 minutes when a test concentration of 692 ppm was sampled at a flow rate of 0.105 liter/min.

Discussion

Desorption efficiency trials on charcoal Lot 105 were conducted in order to select an appropriate desorbing solvent. Six hundred mg portions of charcoal were spiked with 0.310 mg of methyl chloride as described in NIOSH Method S99. Carbon disulfide, chloroform, ethanol, and methylene chloride were tested as possible desorbing solvents. The following results were obtained.

Table S99-2

Desorption Efficiency Trials

Desorbing Solvent	Recovery from Charcoal
Carbon disulfide	78%
Chloroform	67%
Ethanol	89%
Methylene chloride	100%

From the above results, methylene chloride was selected as the desorbing solvent.

Independent Method

The "taken" concentration for the T.W.A. and peak concentrations in the generator were determined based on measured flow rates of methyl chloride from the gas cylinder and the amount of dilution air used to reach the desired concentrations. The following data were obtained:

Table S99-3

"Taken" Concentrations

Level	T.W.A.	Peak
0.5X	54.2	146.6
1X	108.4	318
2X	223	590

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2. A summary is given in Attachment C.

The precision of the analytical method was assessed using the data in Table S99-4. The pooled Coefficient of Variation (CV_1) for the three sets of analytical samples were found to be 0.016.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S99-5 (T.W.A.), and the results obtained from breakthrough tests and storage stability tests. The data in Table S99-5 did not pass Bartlett's test at the 1% confidence level. Chi squared was calculated to be 16.1. Therefore, the data was not pooled for the calculation of CV_T. CV_2 at the 1X level was used to calculate CV_T by the following equation

$$CV_T = \sqrt{CV_2^2 \text{ (1X level)} + (0.05)^2}$$

where 0.05 is equivalent to the pump error. CV_T was calculated to be 0.052.

The average recovery (conc. found/conc. taken) for the three levels at the T.W.A. concentration was 105.2%. The average recovery for the three levels at the peak concentration was 101%. 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 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.

Table S99-4

Data Sheet: Methyl Chloride

Analysis

Level

mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
0.1550	0.1494	0.964	0.310	0.308	0.994	0.620	0.610	0.984
0.1550	0.1508	0.973	0.310	0.315	1.016	0.620	0.615	0.992
0.1550	0.1499	0.967	0.310	0.310	1.000	0.620	0.616	0.994
0.1550	0.1510	0.974	0.310	0.312	1.006	0.620	0.617	0.995
0.1550	0.1451	0.936	0.310	0.313	1.010	0.620	0.623	1.005
0.1550	0.1566	1.010	0.310	0.314	1.013	0.620	0.624	1.007
n =		6			6			6
mean		0.971			1.006			0.996
std dev		0.024			0.008			0.009
CV_1		0.025			0.008			0.009

$\overline{CV_1}$ 0.016

$\overline{CV_{A+\overline{DE}}}$ 0.017

From the above results, no correction for desorption efficiency (D.E.) is necessary in Tables S99-5 and S99-6.

Table S99-5

Data Sheet: Methyl Chloride (T.W.A.)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Liters	mg/cu m	ppm*	ppm	Percent Recovery
0.5X	0.1982	1.674	118.4	57.3	54.2	
	0.1766	1.506	117.3	56.8	54.2	
	0.1951	1.592	122.6	59.3	54.2	
	0.1834	1.496	122.6	59.3	54.2	
	0.1983	1.582	125.4	60.7	54.2	
	0.1977	1.602	123.4	59.7	54.2	
			n = 6			
			mean	58.9		108.7
			std dev	1.5		
			CV_2	0.025		
1X	0.371	1.518	244.4	118.3	108.4	
	0.374	1.548	241.6	116.9	108.4	
	0.333	1.398	238.2	115.3	108.4	
	0.362	1.535	235.8	114.1	108.4	
	0.368	1.529	240.7	116.5	108.4	
	Sample was lost.					
			n = 5			
			mean	116.2		107.2
			std dev	1.6		
			CV_2	0.014		
2X	0.671	1.535	437	212	223	
	0.664	1.497	444	215	223	
	0.581	1.439	404	196	223	
	0.891	1.614	552	267	223	
	0.655	1.468	446	216	223	
	0.706	1.523	464	225	223	
			n = 6			
			mean	222		99.6
			std dev	24		
			CV_2	0.108		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference 2.

The results for the three levels cannot be pooled, because the results failed Bartlett's test for homogeneity.

Table S99-6

Data Sheet: Methyl Chloride (Peak, 5-minute sample)

Sampling and Analysis

Test Level	Found				Taken	
	mg	Liters	mg/cu m	ppm*	ppm	Percent Recovery
0.5X	0.1622	0.529	307	148.6	146.6	
	0.1537	0.533	288	139.4	146.6	
	0.1589	0.532	299	144.7	146.6	
	0.1573	0.536	293	141.8	146.6	
	0.1510	0.526	287	138.9	146.6	
	0.1582	0.520	304	147.1	146.6	
			n = 6			
			mean	143.4		97.8
			std dev	4.0		
			CV_2	0.028		
1X	0.374	0.524	714	346	318	
	0.356	0.523	681	330	318	
	0.367	0.535	686	332	318	
	0.382	0.537	711	344	318	
	0.401	0.546	734	355	318	
	0.371	0.550	675	327	318	
			n = 6			
			mean	339		106.6
			std dev	11		
			CV_2	0.032		
2X	0.660	0.531	1243	602	590	
	0.628	0.525	1196	579	590	
	0.639	0.523	1222	591	590	
	0.640	0.525	1219	590	590	
	0.584	0.531	1100	532	590	
	0.669	0.540	1239	600	590	
			n = 6			
			mean	582		
			std dev	26		98.6
			CV_2	0.045		

*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, NIOSH Contract CDC-99-74-45.

Attachment A

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 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

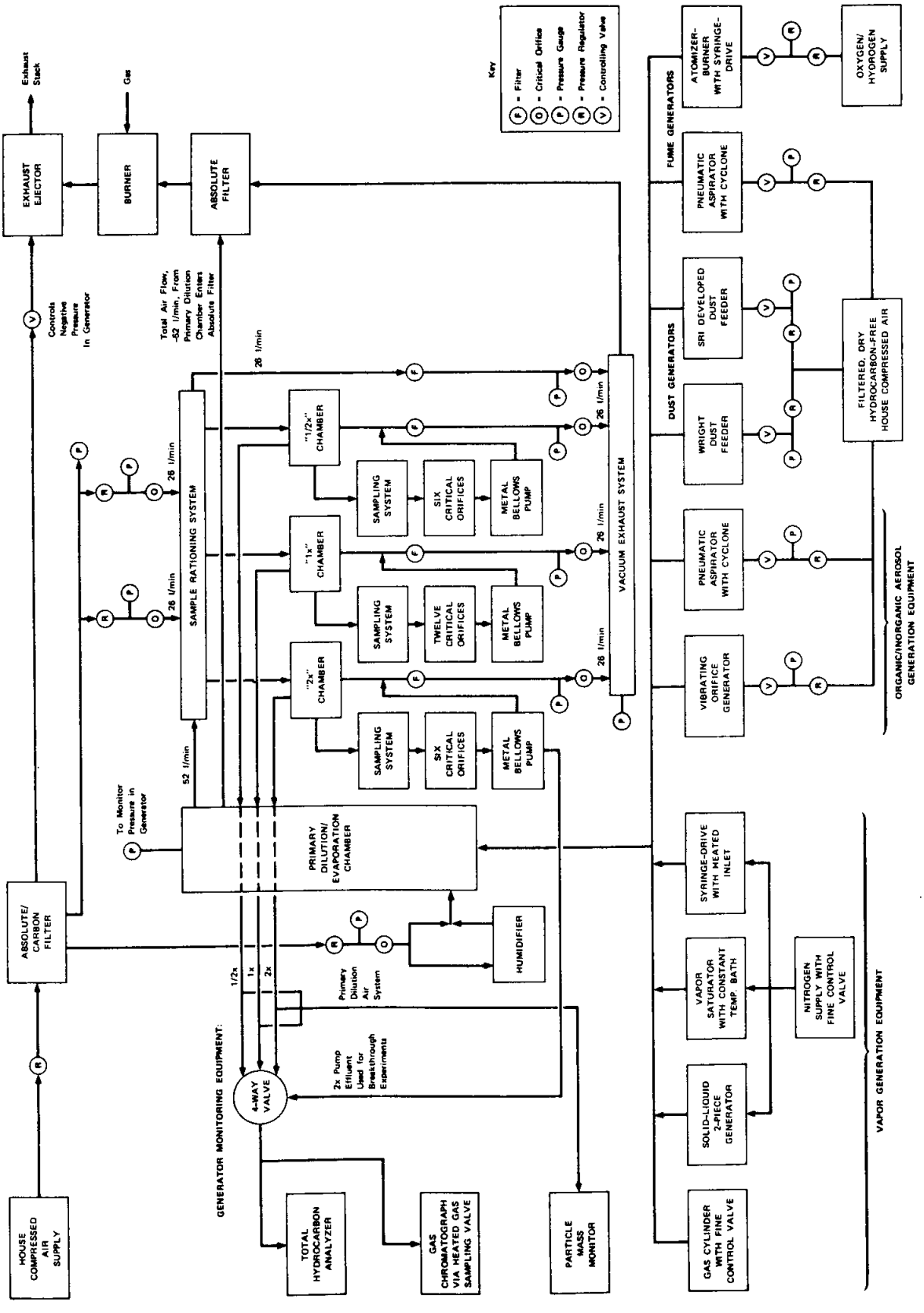


Figure S99-A1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

(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.

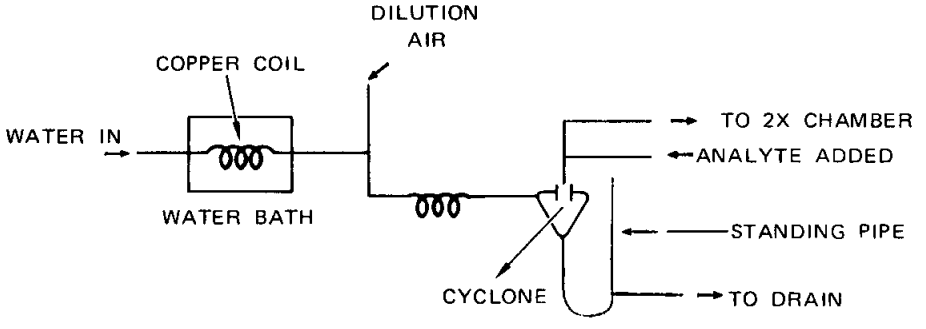
The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected 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 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 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.

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 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.

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

$\overline{CV}_2$ - 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:

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

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.

Stibine

Analyte:	Stibine	Method No.:	S243
Matrix:	Air	Range:	0.119-1.008 mg/cu m
OSHA Standard:	0.1 ppm (0.5 mg/cu m)	Precision (CV_T):	0.087
Procedure:	Collection on mercuric chloride-coated silica gel, acid extraction, colorimetry/Rhodamine B.	Validation Date:	3/18/77

1. Principle of the Method

1.1 A known volume of air is drawn through a mercuric chloride impregnated silica gel tube to trap the stibine.

1.2 The antimony is extracted from the treated silica gel using concentrated hydrochloric acid.

1.3 An aliquot of the extracted sample is analyzed for antimony by oxidation of all of the antimony to Sb(V), extraction into isopropyl ether and formation of the Rhodamine B complex. The absorbance of the complex is measured at 552 nm. The absorbance is proportional to the antimony concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.119-1.008 mg/cu m at an atmospheric temperature and pressure of 21°C and 769 mm Hg, respectively, using a 20-liter sample.

2.2 Sampling at 0.2 liters per minute for 90 minutes will yield an 18-liter sample. The working range for a sample of this size is estimated to be 0.1-1.5 mg/cu m.

2.3 The method may be extended to higher concentrations by further dilution of the extracted sample; however, the maximum capacity of the collection tube has not been established. Based on the breakthrough data, a level as high as 3.89 mg/cu m may be determined.

3. Interferences

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

3.2 The colorimetric determination of antimony is subject to interference by any element which also forms a Rhodamine B complex which is extractable into isopropyl ether. Species such as Am(III) (>250 µg), Au (>1000 µg), Fe(III) (>30,000 µg), Tl(I) (> 1000 µg), and Sn(II) (>1000 µg) have been reported (Reference 11.1) to give interference. If the presence of these elements is suspected, their concentration in the extracted solution should be determined to evaluate their effects on the antimony data.

3.3 If the possibility of interferences do exist, modification of the analytical procedure must be made to circumvent the problems or an alternative procedure should be used.

4. Precision and Accuracy

4.1 The Coefficient of Variation $\overline{CV}_T$ for the total sampling method in the range 0.119-1.008 mg/cu m was 0.087. This value corresponds to a standard deviation of 0.0435 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3. Since no analytical set or desorption efficiency data were obtained, the CV_T value is based only on the generated set data and pump error.

4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analytical procedure was 0.7% higher than the average taken concentration for a limited number of laboratory experiments. Any difference between the found and taken concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined taken ("true") concentration. Thus no recovery corrections should be applied to the final result.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids.

5.2 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 only one tube.

5.3 The analytical method requires that once the analysis of an extracted sample is started, it be carried out to completion on each individual sample. This may present an inconvenience. However, the complete analysis can and should be completed within 15 minutes.

6. Apparatus

6.1 A calibrated personal pump whose flow can be determined within ± 5% of the recommended flow rate. The pump must be calibrated with a representative tube in the line.

6.2 Treated silica gel tube. Glass tube with both ends flame sealed, 2.5 in. long with 8-mm O.D. and 6-mm. I.D., containing 2 sections of treated silica gel (grade 43, 14/20 mesh, Indicator type, Davison-Grace Co.) The adsorbing section contains 1.0g of treated silica gel and the backup 0.5g. A small wad of silylated glass wool is also 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. The silica gel is coated according to the following procedure:

6.2.1 Dry one hundred grams of silica gel at 100°C for 2 hours.

6.2.2 Prepare a 10% w/v mercuric chloride solution in methyl alcohol.

6.2.3 Add the dried silica gel to the mercuric chloride solution and let sit for 15 minutes with occasional stirring.

6.2.4 Drain the excess mercuric chloride solution and dry the remaining silica gel at 80°C for 3 hours.

6.2.5 Cool the silica gel to room temperature in a covered beaker.

6.2.6 Expose the tube to a humid atmosphere until the indicator turns pink.

6.3 A spectrophotometer capable of measuring absorbance or transmittance at 552 nm.

6.4 Two matched 1-cm silica cells with tight fitting Teflon caps.

6.5 Separatory funnel, 125 ml.

6.6 Beakers, 50 ml.

6.7 Volumetric flasks, 25, 50, 250, and 500 ml.

6.8 Pipets. 15 and 20-ml and other convenient sizes to make standard dilutions.

6.9 Graduated cylinders, 10 and 25 ml.

6.10 Laboratory centrifuge with two 15-ml centrifuge tubes with tight-fitting caps. (Do not use rubber stoppers).

6.11 Balance.

6.12 Barometer.

6.13 Thermometer.

6.14 Stopwatch.

7. Reagents

All reagents should be ACS reagent grade or better.

7.1 Hydrochloric acid, concentrated.

7.2 Antimony standard solution, 1000 ppm. (Commercially available)

7.3 Ceric sulfate, $Ce(SO_4)_2$, solid.

7.4 Isopropyl ether, low in alcohol and water.

7.5 Water, distilled or deionized.

7.6 Rhodamine B.

7.7 Stock Rhodamine B solution, 0.2% in water. Prepare by dissolving 0.5 g in 250-ml volume.

7.8 Working Rhodamine B Solution, 0.01% in 0.5 M HCl. Prepare by mixing 25 ml of the stock Rhodamine B solution and 24 ml of concentrated HCl in 500 ml volume. Prepare fresh daily.

8. Procedure

8.1 Cleaning of equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6M nitric acid, tap water, distilled water in that order and then dried. Important: if acetone is used to dry the glassware, it is imperative that no residual acetone be present. The glassware should be perfectly dry.

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 6.2. 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 two ends of the silica gel tubes to provide an opening of at least one half of the internal diameter of the tube (3 mm).

8.3.2 The treated silica gel tubes should be placed in a vertical direction during sampling to minimize channeling through the gel.

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

8.3.4 A sample size of 18 liters is recommended. Sample at a known flow rate of 0.2 liters per minute or less for 90 minutes. The flow rate should be known with accuracy of at least ± 5%.

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

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

8.3.7 With each batch of 5 samples, submit one treated silica gel tube which had been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.

8.3.8 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 silica gel tube is scored with a file and broken open. The glass wool is removed with care and discarded making sure that no silica gel is lost in the process. The silica gel in front is transferred to a 50 ml beaker. The separating section of glass wool is removed and discarded. The backup section of silica gel is transferred to another container. These two sections are analyzed separately.

8.4.2 Extraction of the sample. Prior to analysis, 15 ml of concentrated HCl is pipetted into each beaker containing the silica gel. The extraction is carried out for 30 minutes at room temperature with occasional swirling during this period. After extraction the hydrochloric acid solution is drained into a 25 ml volumetric flask leaving the silica gel. The remaining gel is washed twice with 4 ml portions of concentrated HCl and the washings are drained and added to the volumetric flask containing the initial extract solution. The extract and washings are made up to volume with concentrated HCl and thoroughly mixed.

8.4.3 Spectrophotometer operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 552 nm and set the zero and 100% transmittance scale using a 1 cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

Note: Steps 8.4.4.1 through 8.4.4.10 should be performed within a 15 minute period.

8.4.4.1 Pipet 15 ml of the extracted sample into a 125 ml separatory funnel.

8.4.4.2 Add 10-20 mg (spatula tip) ceric sulfate. Swirl to dissolve the solid and let stand for 60 seconds unstoppered.

8.4.4.3 Pipet 15 ml of isopropyl ether into the funnel, stopper and shake for 30 seconds, releasing the pressure only at the beginning and end of that period.

8.4.4.4 Add 7 ml of water, shake for 60 seconds. Allow 60 seconds for the aqueous and non-aqueous layers to separate and discard the lower (aqueous) layer.

Note: It is important to remove all of the aqueous layer and that none remains in the stopcock.

8.4.4.5 Pipet 20 ml of the working Rhodamine B solution. Shake for 60 seconds, releasing the pressure only at the beginning and end of that period.

8.4.4.6 Allow 60 seconds for the two phases to separate. Discard the lower (aqueous) layer.

8.4.4.7 Drain 10 ml of the isopropyl ether solution into a 15 ml centrifuge tube and cap tightly to prevent any evaporation of the ether.

8.4.4.8 Centrifuge for 120 seconds at 2000 RPM.

8.4.4.9 Transfer the sample into a 1 cm absorption cell and stopper immediately.

8.4.4.10 Measure the absorbance or transmittance at 552 nm using isopropyl ether as a blank.

9. Calibration and Standards

9.1 Using the standard antimony solution, prepare at least six calibration standards in concentrated HCl to cover the antimony concentration 2 to 20 µg Sb per 15 ml.

9.2 Prepare these standards fresh daily by appropriate dilution of the stock using concentrated HCl for all dilutions. A blank containing no antimony should also be analyzed.

9.3 Proceed as in Sections 8.4.4.1 to 8.4.4.10.

9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the blank versus the concentration of each standard in µg Sb per 15 ml on linear graph paper.

10. Calculations

10.1 Correction for the blank (obtained by extraction and analysis of the silica gel tube marked "blank") must be made for each sample.

$$Abs_{corr} = Abs_{sample} - Abs_{blank}$$

10.2 Read the amount of antimony, in µg Sb per 15 ml, corresponding to the Abs_{corr} from the standard curve.

10.3 Multiply the total weight of antimony by 1.708 to obtain the corrected µg SbH_3 per 25 ml sample.

$$\mu g\ SbH_3 \text{ in sample} = \mu g\ Sb \times 1.708$$

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 appropriate information, such as the 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 (liters per minute)

t = sampling time (minutes)

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 analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{corrected µg } SbH_3 \text{ (Section 10.4)}}{\text{volume of air sampled in liters}}$$

11. References

11.1 F. N. Ward and H. W. Lakin, Analytical Chem., 26, 1168 (1954).

11.2 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.

11.3 S243 Backup Data Report for Stibine, prepared under NIOSH Contract No. 210-76-0123, 3/18/77.

Sampling Data Sheet No. S243

Substance

Stibine

OSHA Standard

8-hour time weighted average: 0.1 ppm (5 mg/cu m)

Analytical Method

A known volume of air is drawn through mercuric chloride-coated silica gel to trap the stibine gas. The antimony is extracted from the treated silica gel with concentrated hydrochloric acid and analyzed colorimetrically after formation of a Rhodamine B-antimony complex. The method has been validated over the range 0.119-1.008 mg/cu m for a 20-liter sample at 21°C and 769 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The sampling equipment needed consists of a sampling tube filled with mercuric chloride-coated silica gel and a personal sampling pump calibrated with a representative gel tube in the line. The pump flow rate should be determined accurately to $\pm$ 5% at the sampling rate used. A suitable tube holder should be used to protect the worker from the sharp edges of the glass sampling tube.

The treated silica gel tube used to collect the sample consists of a glass tube, flame sealed at both ends, 2.5 in. long with an 8-mm O.D. and 6-mm I.D., packed with two sections of mercuric chloride-coated silica gel (14/20 mesh). The two sections include a front section containing 1.0 g of treated silica gel and a backup section containing 0.5 g. 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 of mercury at a flow rate of 1 liter per minute.

The mercuric chloride-coated silica gel is prepared as described. Dry one hundred grams of silica gel at 100°C for 2 hours. Meanwhile, prepare a 10% w/v mercuric chloride solution in methyl alcohol. Add the dried silica gel to the mercuric chloride solution and let sit for 15 minutes with occasional stirring. Drain the excess mercuric chloride solution and dry the remaining silica gel at 80°C for 3 hours. Cool the silica gel to room temperature in a covered beaker. Expose the tube to a humid atmosphere until the indicator turns pink.

Sample Size

A sample size of 18 liters is recommended. Sample at a known flow rate of 0.2 liter per minute or less for 90 minutes. Do not sample at a flow rate less than 0.01 liter per minute.

Sampling Procedure

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

2. The section containing 0.5 g of treated silica gel is used as a backup and should be positioned nearest to the sampling pump. The silica gel tube series should be placed in a vertical position during the 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 treated silica gel 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 the 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 capped with the supplied 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. 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 10 samples.

Special Considerations

1. Other air contaminants may interfere with the analysis. These species have been reported as interferences: americium (III), gold, iron (III), thallium (I), and tin (II). The suspected presence of these elements and other air contaminants should be transmitted with the samples.

2. Sample for no more than eight hours without recharging the battery to avoid drainage of pump battery.

3. Because breakthrough experiments were conducted at a relative humidity of 85%, further reductions in sample volume should not be needed. However, when water condenses on the solid sorbent, the analyte may not be trapped quantitatively.

Shipping Instructions

Capped treated silica gel 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

Stibine, NIOSH Method S243.

Backup Data Report No. S243

Substance: Stibine

OSHA Standard: 0.1 ppm (0.5 mg/cu m)

Chemicals Used for Validation: $SbCl_3$, Fisher Scientific
$SbOC_4H_4O_6 \cdot 1/2H_2O$, Fisher Scientific

General Considerations

The method for stibine 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 stibine consisted of the following experimental studies:

- Evaluation of the Rhodamine B method of analysis for antimony,
- Development of a method for independent verification of the stibine concentration,
- Evaluation of collection by mercuric chloride coated silica gel relative to efficiency, breakthrough and storage stability,
- Analysis of 24 samples (6 samples at each of four test levels -- 0.238X, 0.720X, 1.330X and 2.070X the OSHA standard) collected from dynamically generated test atmospheres,
- Verification of collection efficiency at a high relative humidity at two test levels (0.990X and 2.65X the OSHA standard),
- Analysis of three collected samples using hydride evolution and atomic absorption to check the Rhodamine B method,
- Testing of the storage stability of collected samples,
- Assessing 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 the Method

The method validated for the analysis of stibine in air is based on collection on mercuric chloride coated silica gel, extraction of the antimony from the gel using concentrated acid and analysis by colorimetry using Rhodamine B. A sample size of 18 liters is recommended.

Analytical Method

A detailed description of the procedure for analysis and the preparation of calibration standards are given in NIOSH Method No. S243 (Reference 3). A set of analytical samples was not prepared due to the inability to spike with SbH_3. The use of any other antimony compound as a spike is not justified since the chemical form of the antimony on the mercuric chloride coated silica gel ($HgCl_2$/silica gel) would not be equivalent to that which occurs when stibine reacts with $HgCl_2$. The reliability of the Rhodamine B method for analysis of antimony was established by checking the effects of the following:

a. Stability of the absorbance with time,

b. Presence of mercuric chloride (5000 ppm),

c. Amount of added cerium (IV) oxidant (5 vs. 50 mg),

d. Time of oxidation (15 seconds vs. 60 seconds,

e. Source of antimony ($SbCl_3$ vs. $SbOC_4H_4O_6 \cdot 1/2H_2O$),

f. Comparison of the results with those obtained using SbH_3 evolution and subsequent analysis by atomic absorption,

g. Linearity of the calibration curve over the working range (2-20 µg Sb).

The results are discussed below.

The absorbance reading obtained in the analysis of 20 µg of Sb was found to be stable for 1 hour but decreased rapidly over the next 3 hours. After 4 hours the absorbance was only about 60% of its initial value. The absorbance of the Rhodamine B-antimony complex was thus measured immediately after color development in all cases.

No significant variation in absorbance readings were observed in the presence of mercuric chloride as shown by the following data:

Absorbance Data in the Presence and Absence of $HgCl_2$

Sample	Absorbance
4.00 µg Sb	0.323
4.00 µg Sb + 5000 ppm $HgCl_2$	0.315
10.00 µg Sb	0.800
10.00 µg Sb + 5000 ppm $HgCl_2$	0.815

Similarly, variations in the amount of oxidant and in the amount of time allowed for oxidation has no significant effect, as shown below:

Absorbance Data for Various Amounts of Oxidant and Various Oxidation Times

Sample	Absorbance
10 µg Sb + 5 mg Ce(IV)	0.805
+ 10 mg	0.789
+ 20 mg	0.821
+ 50 mg	0.813
10 µg Sb + 10 mg (15 sec. oxidation)	0.789
+ 10 mg (30 sec. oxidation)	0.789
+ 10 mg (60 sec. oxidation)	0.780

The method was also shown to give similar results for equivalent amounts of antimony independent of the initial chemical form of the added antimony as shown below:

Comparison of Data Obtained Using $SbCl_3$ and $SbOC_4H_4O_6$

µg Sb Added	Absorbance
3.90[a]	0.323
3.90[b]	0.315
5.00[a]	0.423
5.00[b]	0.431
9.50[a]	0.789
9.50[b]	0.797

[a]Added as $SbCl_3$

[b]Added as $SbOC_4H_4O_6$

An independent check of the antimony concentration was also obtained by analyzing samples of stibine collected both on $HgCl_2$/silica gel tubes and in impingers containing 5000 ppm $HgCl_2$ in concentrated HCl (see: Independent Method for Verifying Generator Concentration) by both the Rhodamine B method and by SbH_3 evolution and subsequent

analysis by atomic absorption (SbH_3/AA -- See Attachment A). Good agreement was observed between the results obtained using these two methods, as shown below:

Comparison of Results Obtained Using Rhodamine B and SbH_3/AA

µg Sb found Rhodamine B	µg Sb found SbH_3/AA	% Found (SbH_3/AA ÷ Rhodamine B)
17.8	18.3	102.8
20.3	19.4	95.6
21.3	22.3	104.7
		Avg: 101.0%

A calibration curve was constructed according to the prescribed procedure described in NIOSH Method No. S243, using standards prepared from $SbCl_3$. The straight line fitted to the data by the method of least squares linear regression had a correlation coefficient of 0.997 over the working range 2-20 µg Sb. The observed absorbances for this range cover the region between 0.166 - 1.66 absorbance units.

Detection Limit

The detection limit for the determination of antimony using the Rhodamine B method was taken to be twice the standard deviation obtained from the absorbance data of a set of 6 determinations of blank samples of $HgCl_2$/silica gel tubes. The data are shown below:

Sample	Absorbance
1	0.045
2	0.050
3	0.023
4	0.047
5	0.042
6	0.040
n = 6	
mean	0.041
std. dev.	0.010

The detection limit thus corresponds to 0.02 absorbance units or 0.246 µg of SbH_3 per 15 ml of sample. This translates to a detection limit of 0.410 µg of SbH_3 per 25 ml of solution.

Sampling and Analysis

Stibine was produced by reduction of antimony (added as $SbOC_4H_4O_6$) with sodium borohydride in acid solution according to the following reaction (Reference 6):

$$3\ BH_4^- + 4\ H_3SbO_3 + 3H^+ \rightarrow 3H_3BO_3 + 4SbH_3\uparrow + 3H_2O$$

Test atmosphere samples were generated using the basic system described in Attachment B. A steady stream of antimonite solution, prepared by adding 1.5 g potassium antimony tartrate, 22.5 g of 45% potassium hydroxide, 1.4 g sodium borohydride powder and 1 g tartaric acid to water and diluting to 100 ml, was delivered at various known rates into a three-necked 250-ml round bottom flask containing 50-100 ml of 4N sulfuric acid. The stibine produced (References 4, 5 and 6) was flushed out of the reaction vessel with a steady stream of nitrogen (1 liter per minute) into the main dilution system where it was further diluted with 100 liters per minute flow of air. Since the reaction to produce SbH_3 is not quantitative (Reference 5) and was not found to be sufficiently reproducible under identical generation conditions (see Generation Difficulties), it was necessary to determine the stibine concentration directly in the test atmosphere by an independent collection method using impingers simultaneously with the sampling process being evaluated. The taken concentrations were derived from the impinger data and are described in detail in the section labeled Independent Method for Verifying Generator Concentration.

The generated samples were collected using 1 g of $HgCl_2$/silica gel tubes described in Section 6.2 of NIOSH Method No. S243. The 24 samples, 6 each at four test levels, were collected in four separate experiments. These samples were analyzed as described in Section 8.4 of NIOSH Method No. S243. The data obtained for these samples are shown in Table S243-1.

Storage Stability

Studies were done to assess the stability of collected stibine samples upon storage for one week at atmospheric conditions. For these studies 12 samples were collected from one test atmosphere, six were analyzed within 1 day of sampling, and the results were compared with the data obtained for the remaining samples analyzed after storage for seven days. The data obtained for these samples are shown in Table S243-2. These results indicate that the samples are stable for seven days; the average value found for samples analyzed within 1 day was 0.671 mg/cu m vs. 0.662 mg/cu m obtained from seven-day-old samples.

Collection Efficiency and Breakthrough Tests

Tests of collection efficiency and breakthrough were performed in an atmosphere of 85% relative humidity. These tests were conducted at two test levels (1.1X and 2.65X the OSHA standard) at two sampling

TABLE S243-1

Data Sheet: Stibine, S243

Sampling and Analysis

Test Level	Found			Taken *	
0.24S	µg	Liters	mg/cu m	mg/cu m	Recovery
	2.590	20.43	0.127	0.1193	
	1.310**	20.43	0.064	0.1193	
	2.480	19.89	0.125	0.1193	
	2.150	19.89	0.108	0.1193	
	1.660	15.30	0.108	0.1193	
	2.010	19.40	0.104	0.1193	
		n = 5			
		mean	0.1144		
		std dev	0.01074		0.959
		CV_2	0.0939		
0.72S	7.46	19.80	0.377	0.361	
	4.63	15.30	0.303	0.361	
	6.78	19.98	0.339	0.361	
	6.41	20.07	0.319	0.361	
	6.83	20.25	0.337	0.361	
	6.80	19.98	0.340	0.361	
		n = 6			
		mean	0.336		
		std dev	0.02484		0.931
		CV_2	0.0739		
1.3S	13.58	19.89	0.683	0.666	
	13.18	19.98	0.660	0.666	
	14.07	20.43	0.689	0.666	
	13.46	19.80	0.680	0.666	
	12.64	19.62	0.644	0.666	
	10.68**	19.89	0.537	0.666	
		n = 5			
		mean	0.671		
		std dev	0.01870		1.008
		CV_2	0.02787		

(Table continued on next page)

TABLE S243-1 (continued)

2.1S	19.22	19.98	0.962	1.033	
	22.07	19.89	1.110	1.033	
	22.86	19.89	1.149	1.033	
	16.99	15.30	1.110	1.033	
	22.02	21.06	1.046	1.033	
	23.33	19.80	1.178	1.033	
		n = 6			
		mean	1.092		
		std dev	0.0778		1.058
		CV_2	0.0712		
		$\overline{CV}_2$	0.0711		

Notes to Table S243-1

* Data obtained by collection in impingers. See Independent Method for Verifying Generator Concentration.

** Not included in the statistical analysis. Rejected using Grubb's test.

TABLE S243-2

Data Sheet: Stibine, S243

Studies in Stability of Collected Samples

Experiment A: Samples Analyzed Within 1 Day of Collection

Test Level*	----------Found----------				
1.3S	µg	Liters	mg/cu m	Taken* mg/cu m	Recovery
	13.58	19.89	0.683	0.666	
	13.18	19.98	0.660	0.666	
	14.07	20.43	0.689	0.666	
	13.46	19.80	0.680	0.666	
	12.64**	19.62	0.644	0.666	
	10.68**	19.89	0.531	0.666	
		n = 5			
		mean	0.671		
		std dev	0.01870		1.008
		CV_2	0.02786		

Experiment B: Samples Analyzed After Storage for 7 Days

Test Level	----------Found----------				
1.3S	µg	Liters	mg/cu m	Taken* mg/cu m	Recovery
	13.05	19.51	0.669	0.666	
	12.30	18.72	0.657	0.666	
	14.26	21.38	0.667	0.666	
	13.31	21.03	0.633	0.666	
	13.31	19.07	0.698	0.666	
	13.21	20.32	0.650	0.666	
		n = 6			
		mean	0.662		
		std dev	0.02181		0.994
		CV_2	0.0330		

* Data obtained by collection in impingers. See Independent Method for verifying generator concentration.

** Not included in the statistical analysis. Rejected using Grubb's test.

times (120 and 240 minutes) by using a front and a backup tube; the sampling rate was 0.22 liters per minute. The results obtained for these experiments are presented in Table S243-3. These data indicate that breakthrough did not occur in 240 minutes. (Breakthrough is defined as the time when 5% of the inlet concentration of the analyte is observed in the sample after passage through the collection tube.) The capacity of the collection tube is therefore greater than 70 µg (as SbH_3).

Generation Difficulties

The generation of a predetermined test atmosphere of stibine was hampered by the irreproducibility of the yield of the reaction between potassium antimony tartrate and sodium borohydride in acid solution. A comparison of the amount of SbH_3 produced to the total amount of antimony added to the reaction vessel is made in Table S243-4 and illustrates this irreproducibility. These variations in stibine production may be attributed to the production of Sb metal during the course of the reaction. The yield of antimony metal is apparently not constant, presumably due to further reaction to produce stibine. The varying rate of this reaction may be the source of the variations observed in the total yield of stibine.

The initially produced test atmospheres for the generated samples did not meet the primary requirements set forth in the statement of work (Reference 1) that the three levels must be within 25% of 0.5X, 1.0X and 2.0X the OSHA standard. It was thus necessary to produce a fourth level to meet the alternative requirements.

The generation difficulties have little implication on the validity of the sampling and analytical method since an independent method of determining generator concentration was used. This method is described in the following section.

Independent Method for Determining Generator Concentration

The method used to determine the stibine concentration in the test atmosphere was collection of stibine in impingers containing 0.5% $HgCl_2$ in concentrated HCl (Reference 7) and analyzing for antimony using Rhodamine B. The collection efficiency of this method was tested by using front and backup impingers under a variety of conditions. These data are presented below.

TABLE S243-3

Collection Efficiency of Stibine on $HgCl_2$/Silica Gel

Experiment A: Sampling Condition: 120 minutes at approximately 0.22 liter per minute

Test Concentration

mg SbH_3/cu m	μg SbH_3 found			% Collected in Front Tube
	Front Tube	Backup Tube	Total	
0.590	17.59	N.D.[a]	17.59	100
	17.24	N.D.[a]	17.24	100
	16.73	N.D.[a]	16.73	100
	35.30	N.D.[a]	35.30	100
1.339	38.06	N.D.[a]	38.06	100

Average Collection Efficiency 100**

Experiment B: Sampling Condition: 240 minutes at approximately 0.22 liter per minute

mg SbH_3/cu m	μg SbH_3 found			% Collected in Front Tube
	Front Tube	Backup Tube	Total	
0.499	26.98	N.D.[a]	26.98	100
	27.49	N.D.[a]	27.49	100
	28.48	N.D.[a]	28.48	100
	27.33	N.D.[a]	27.33	100
	28.69	N.D.[a]	28.69	100
	27.49	N.D.[a]	27.49	100
1.326	70.39	N.D.[b]	70.39	100
	72.08	N.D.[b]	72.08	100
	73.82	N.D.[b]	73.82	100
	70.39	N.D.[b]	70.39	100

Average Collection Efficiency 100

* The test concentrations reported are based on data from impinger collection.

[a] For these analyses, the detection limit was 0.70 μg Sb.

[b] For these anayses, the detection limit was 1.24 μg Sb.

**The average collection efficiency can also be expressed as at least 96.1% for Experiment A and 95.7% for Experiment B on the basis of the detection limit and the average μg found in the front section.

TABLE S243-4

Yield of SbH_3 from Reaction of $SbOC_4H_4O_6$ with $NaBH_4$

µg Sb added/min	µg SbH_3 produced/min	% Yield
27.02	11.88	42.9
67.28	36.05	52.3
135.1	66.60	48.1
202.4	100.0	48.2
270.2	103.3	37.3
404.8	135.8	32.7

Collection Efficiency of $HgCl_2$/Concentrated HCl-Impingers*

Liters Collected	----Found (μg SbH_3)- Front	Backup	% Collected in Front
11.00	9.43	N.D.	100
11.05	9.53	N.D.	100
10.85	10.35	N.D.	100
20.07	7.64	N.D.	100
18.90	17.93	N.D.	100
	Average Collection Efficiency		100**

N.D. = Not Detectable. Detection limit is 0.246 μg SbH_3.
*Average flow rate = 0.22 liters per minute.
**The average collection efficiency is at least 97.6% based on the detection limit and average μg SbH_3 found in the front impinger.

The test atmosphere concentration of stibine was derived from the amount of SbH_3 collected in the impingers and assuming a collection efficiency of 100%. The data used to derive the generator concentrations for the generation and collection efficiency experiments are presented in Table S243-5.

Precision and Accuracy

The precision of the method was determined using the statistical procedures described in Reference 2 and summarized in Attachment C.

Precision and accuracy of the total sampling method was evaluated using the data in Table S243-1. The pooled Coefficient of Variation ($\overline{CV}_2$) for the four sets of samples collected from dynamically generated test atmospheres is 0.0711. The precision of the method is expressed in terms of the coefficient of variation for the overall method which includes a pump error of 0.05. Thus ($\overline{CV}_T$) = 0.0869.

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 four test levels with the taken generator concentrations determined as discussed previously. The data summarized below show good agreement (found ÷ taken) with an average of 98.6%.

Test Level	Taken	Found	Agreement (Found ÷ Taken)
0.238S	0.119	0.114	0.958
0.720S	0.352	0.336	0.931
1.332S	0.666	0.671	1.007
2.070S	1.033	1.082	1.048
		Mean	0.986

TABLE S243-5

Taken SbH_3 Concentrations Based on Impinger Collection Data/
Rhodamine B Method

A. Data for Generated Set: Cross Reference Table S243-1

Liters	µg SbH_3 Found	Test concentration mg/cu m	
19.98	2.50	0.1251	
20.07	2.26	0.1126	
20.25	2.57	0.1269	
19.80	2.24	0.1131	
		n = 4	
		mean 0.1194	(0.238S)
		std dev 0.00763	
		CV 0.0640	
20.07	7.63	0.380	
20.25	6.85	0.338	
19.98	6.97	0.349	
19.80	7.44	0.376	
		n = 4	
		mean 0.361	(0.722S)
		std dev 0.02048	
		CV 0.0567	
17.04	11.11	0.652	
17.76	12.04	0.678	
17.84	11.70	0.656	
18.00	12.47	0.693	
17.76	11.52	0.649	
		n = 5	
		mean 0.666	(1.332S)
		std dev 0.01909	
		CV 0.02866	
19.17	18.75	0.978	
18.90	17.94	0.949	
20.07	19.89	0.991	
20.25	21.36	1.055	
19.98	22.72	1.137	
20.07	21.79	1.086	
		n = 6	
		mean 1.033	(2.066S)
		std dev 0.0720	
		CV 0.0697	

Table continued on next page.

TABLE S243-5, Cont'd.

B. Data for Collection Efficiency Experiments: Cross Reference Table S243-3.

Liters	µg SbH_3 Found	Test concentration mg/cu m		
26.64	15.8		0.593	
27.24	16.0		0.587	
		mean	0.590	(1.180S)
53.76	25.5		0.474	
51.12	23.0		0.450	
53.04	25.0		0.471	
53.28	28.0		0.526	
51.48	28.0		0.544	
53.04	28.0		0.528	
		mean	0.499	(0.998S)
27.24	37.2		1.366	
26.40	34.6		1.311	
		mean	1.339	(2.68S)
52.8	70.6		1.337	
26.4	34.6		1.311	
		mean	1.326	(2.65S)

The difference between the taken and found concentrations is considered to result from experimental uncertainties in the values of the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the method is established by the results of the collection efficiency, breakthrough and storage stability tests described in the appropriate sections.

References

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Attachment A

ANALYSIS OF ANTIMONY USING HYDRIDE EVOLUTION

To check on the accuracy of the Rhodamine B method for determination of total antimony, experiments were performed to determine the antimony concentration in selected samples using a different method. The method used for independent determination of antimony was hydride evolution and subsequent determination by atomic absorption spectrophotometry and has been adapted from References A and B. The work was carried out on a Perkin-Elmer atomic-absorption spectrophotometer, Model 303, with the recorder readout accessory. A Perkin-Elmer antimony electrodeless discharge lamp was used as the light source. The reduction vessel was a pear-shaped flask with a small side opening to allow injection of the reducing solution. An argon-hydrogen-entrained air flame was used with an argon flow of 5 ℓpm through the reaction flask and 18.5 ℓpm to the atomizer. The burner height was 1 cm below the light beam. A wavelength of 217.5 nm and slit width of 3 were used at a scale expansion of 1 and noise suppression of 2.

Standard antimony solutions were prepared by volumetric dilution of "Fisher certified" 1000 ppm antimony standard with concentrated hydrochloric acid. The reduction solution was prepared by dissolving 4 g of $NaBH_4$ (Alfa Products) in 100 mℓ volumetric flask containing 10 g of NaOH pellets (Fisher-certified) and diluting to 100 mℓ with distilled water.

The analysis was carried out by injection of 2.5 mℓ of the borohydride solution to the reaction flask containing 20 mℓ of 6M HCl and 100 µℓ sample in concentrated HCl. Each sample was analyzed in triplicate.

A linear calibration curve was obtained over the range of 0.05-0.2 µg Sb using the above procedure. A comparison of the results obtained for samples analyzed using both the Rhodamine B and SbH_3/AA methods are given below:

Comparison of Results Obtained Using Rhodamine B and SbH_3/AA

µg Sb Found Rhodamine B	µg Sb found[a] Rhodamine B	% Found SbH_3/AA ÷ Rhodamine B
17.8[b]	18.3[b]	102.8
20.3[b]	19.4[b]	95.6
21.3[c]	22.3[c]	104.7
		Average...101.0%

[a]Mean of three measurements. Average standard deviation was 1.2 µg Sb per sample.
[b]Impinger samples.
[c]Extract of $HgCl_2$/silica gel tube.

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B. Fernandez, B.J., At. Absorption Newsletter 12, 93 (1973).

Attachment B

VAPOR GENERATION/DILUTION SYSTEM

The vapor generation/dilution system used for the validation studies of stibine is shown schematically in Figure S243-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 collection tubes or impingers are connected in parallel to each of the 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.

When stibine was generated the system was run without adding any dilution air to the dilution lines so that the same generated atmosphere was present in all of the sampling lines.

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 of 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.

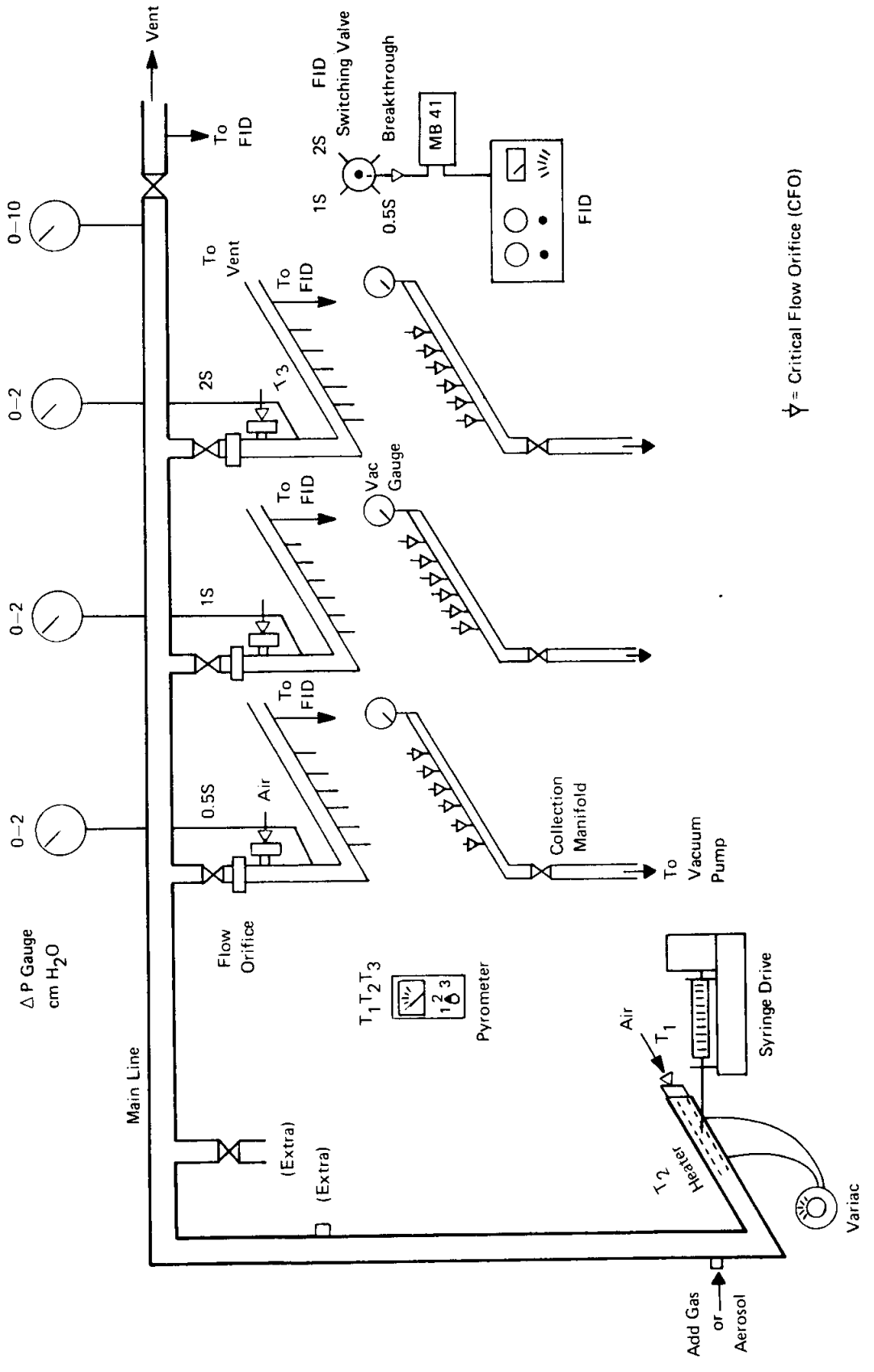

Figure S243-B-1 **VAPOR GENERATION/DILUTION/SAMPLING SYSTEM**

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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.

- as a gas such as from a gas cylinder or a continually purged reaction vessel via an orifice or other flow controller,
- as a liquid via a syringe injector
- as a solid by packing in a glass tower with fritted disc and purging with nitrogen or air.

To generate the stibine test atmospheres, the apparatus shown in Figure S243-B-2 was used. Known amounts of antimonite solution were added at fixed rates to the reaction vessel using a Harvard Model 944 Syringe Drive. A short piece of 1/16-in O.D. Teflon tubing is used to make the connection from the syringe to the reaction vessel. A constant flow of nitrogen (1 liter per minute) is used to flush the gaseous product into the Main Line. The syringe delivery rate is determined as described in the calibration reaction.

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.

Sample Collection Manifold

Sample flow through the collection tubes and impingers connected to the dilution lines is established by connecting each of the tubes by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) 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 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 100 mesh stainless steel screen. When impingers filled with concentrated HCl were used for collection, a backup impinger filled with a solution of sodium hydroxide was also used to protect the CFO.

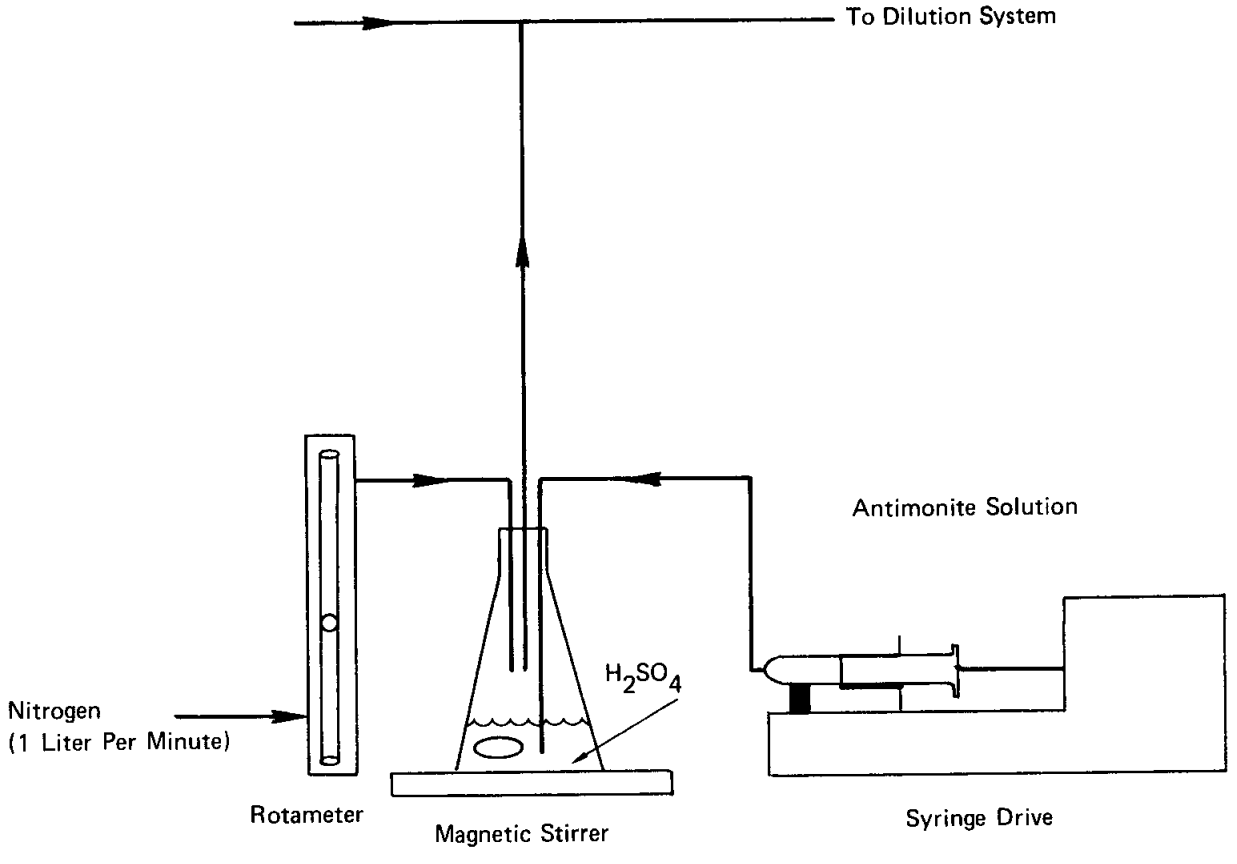

Figure S243-B-2 **APPARATUS USED TO GENERATE STIBINE**

Vent System

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

Calibration

Syringe Drive

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

Air Flows

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

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.

Breakthrough Studies

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 S243-B-3. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 inch x 10 ft) 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 minute to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

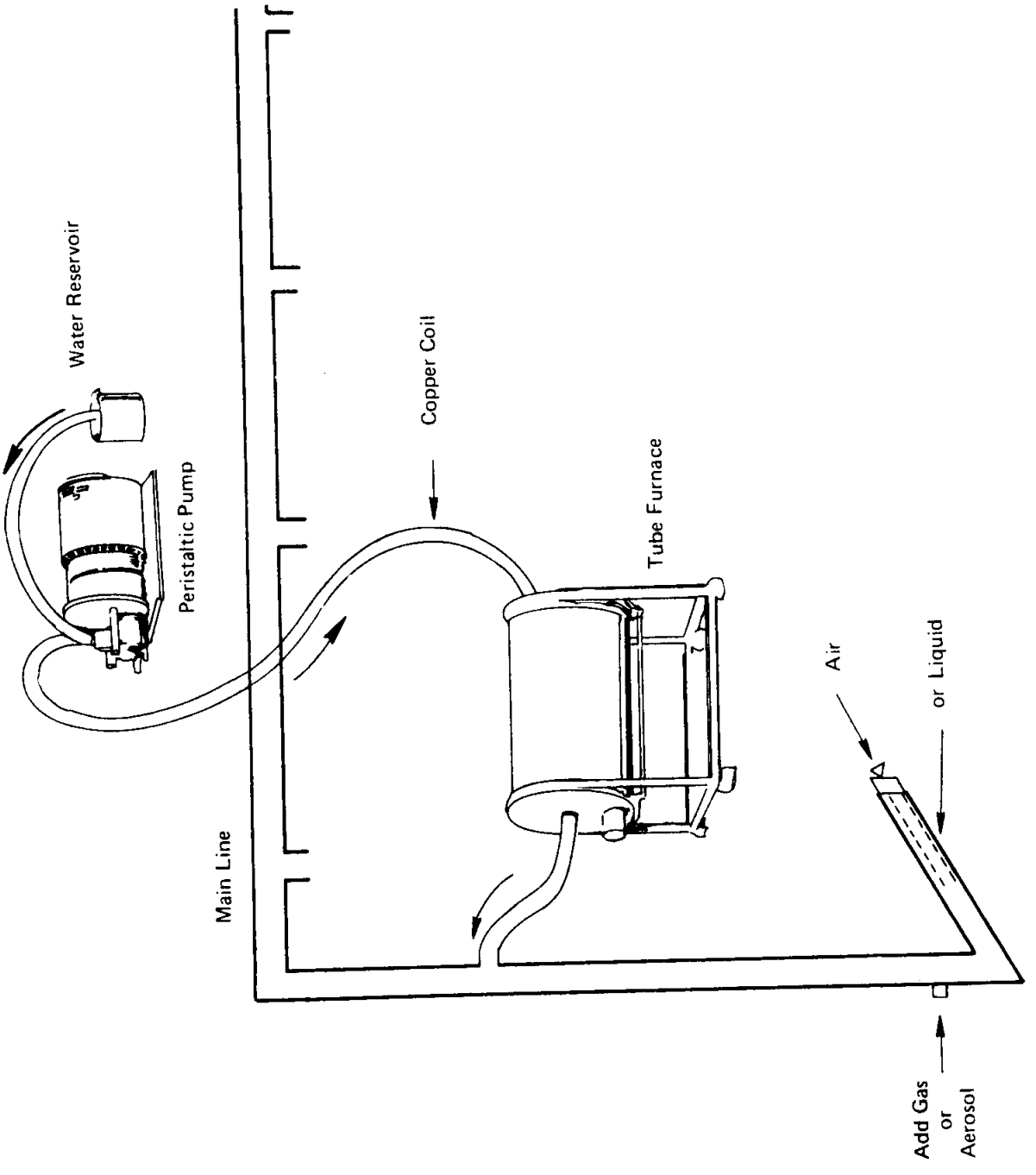

Figure S243-B-3 GENERATION OF HIGH HUMIDITY ATMOSPHERES

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.

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

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

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

$\overline{CV}_2$ - Pooled Coefficient of Variation based on the data for the 18 generated samples.

$\overline{CV}_S$ - Coefficient of Variation of the sample collection, the value is dependent on the data from the 18 analytical and 18 generated samples.

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

$\overline{CV}_P$ - Coefficient of Variation due to the pump error, assumed to be equal to 0.05.

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

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

or:

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

Grubb's Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

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

where:

x = observation being tested

$\bar{x}$ = mean of all observations

s = standard deviation based on n degrees of freedom.

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

Bartlett's Test for Homogeneity of 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:

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

where:

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

$\overline{CV}_{2i}$ = Coefficient of Variation of 6 generated samples at the i^{th} level.

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

$i = 1, 2, 3 \ldots\ldots n$

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

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.

Vanadium, V_2O_5 Fume

Analyte:	Vanadium Oxides	Method No.:	S388
Matrix:	Air	Range:	0.060-0.29 mg/cu m
OSHA Standard:	0.1 mg/cu m - Ceiling	Precision ($\overline{CV}_T$):	0.067
Procedure:	Filter collection, Alkali dissolution, Flameless AAS/HGA	Validation Date:	1/21/77

1. Principle of the Method

1.1 Vanadium oxides sample, collected on mixed cellulose ester membrane filter, is dissolved from the sample-containing filter by heating in a sodium hydroxide solution at 50° C for 15 minutes.

1.2 The solutions of samples and standards are analyzed by flameless atomic absorption spectrophotometry in a high temperature graphite atomizer (HGA). A hollow cathode lamp for vanadium is used to provide a characteristic vanadium line at 318.4 nm. The absorbance is proportional to the vanadium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.060-0.29 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 25-liter sample.

2.2 The OSHA standard for vanadium fume has a 15-minute ceiling value. Sampling at a nominal flow rate of 1.5 liters per minute for 15 minutes will yield 22.5 liters of air sample. For a sample size of 22.5 liters, the working range of the method is estimated to be 0.05-1 mg/cu m.

2.3 The method may be extended to higher values by further dilution of the sample solution; the absolute sensitivity of the method has not been established.

3. Interferences

3.1 There are no known spectral line interferences for the vanadium AAS assay.

3.2 The use of an alkaline dissolution method minimizes the potential interference of ferrovanadium dust.

3.3 Vanadium exhibits self-absorption at 318.4 nm. It is necessary to operate the vanadium hollow cathode lamp at low currents to minimize self-absorption (Reference 11.1).

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the combined analytical and sampling method in the range of 0.060-0.294 mg/cu m was 0.067. This value corresponds to a 0.007 mg/cu m standard deviation at the OSHA ceiling concentration. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2

4.2 A collection efficiency of at least 98.5% was determined for the collection medium; thus, no bias was introduced in the sample collection step. The analytical method recovery was found to be 94.3% with $\overline{CV}_1$ = 0.083. Thus, CV_T is a satisfactory measure of both accuracy and precision. This is supported by data in which x-ray fluorescence was used as an independent method for determining generator concentration. (Reference 11.3).

5. Advantages and Disadvantages

5.1 The method is simple and specific for vanadium oxides (not vanadium metal).

5.2 The method does not distinguish the V_2O_5 dust.

5.3 The life of graphite tubes is limited due to high temperature atomization.

5.4 The calibration curve is non-linear above an absorbance of 0.3 units (ca. 75 ng V_2O_5) and in certain cases, depending on the graphite tube characteristics, it may be necessary to alternate samples with standards of similar response to obtain reliable results.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (section 6.2) and 37-mm 3-piece cassette filter holder.

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. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Barometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have a high temperature graphite atomizer (HGA) and a deuterium arc background corrector.

6.3.1 Vanadium hollow cathode lamp

6.3.2 Deuterium arc lamp

6.3.3 Purge gases: Argon (for HGA), Nitrogen (for Deuterium arc)

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 50-ml beakers with watchglass covers.

6.4.2 Pipetes, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards.

6.4.3 10-ml volumetric flasks

6.5 Water bath maintained at 50°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Water, distilled or deionized

7.2 Sodium hydroxide, 0.01N.

7.3 Standard stock solutions containing 100 µg/ml of vanadium pentoxide. This solution can be prepared by dissolving 0.100 g V_2O_5 in 0.01N sodium hydroxide and diluting to 1.0 liter with 0.01N NaOH.

7.4 V_2O_5 working standard solution, 1.0 µg/ml. Prepare by appropriate dilution of above solution with 0.01N sodium hydroxide. Prepare fresh each day.

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8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6M nitric acid, tap water and distilled or deionized water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect V_2O_5 fume, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute for 15 minutes with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.2 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and 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.

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 50-ml beaker.

8.3.2 V_2O_5 dissolution. To ensure complete dissolution of V_2O_5 from the filter, add 5 ml of 0.01N NaOH to the beaker and heat in a water bath at 50°C for 15 minutes.

8.3.3 Cool solutions and quantitatively transfer the clear solutions into a 10-ml volumetric flask.

8.3.4 Rinse each beaker at least twice with 1-2 ml portions of 0.01N NaOH, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.5 Dilute all samples to 10 ml with 0.01N NaOH.

8.3.6 Inject 50 µl of solution into a high temperature graphite atomizer. Dry at 125°C for 40 seconds, char at 500°C for 10 seconds and atomize at 2700°C for 20 seconds. Use the deuterium arc lamp to correct for "smoke" produced by the by the matrix. Record the absorbance at 318.4 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve if the graphite tube in use gives reproducible results.

NOTE: The characteristics of the graphite tubes can drastically influence the results. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible absorbance peak, it must be rejected and replaced because results so obtained are not reliable. Also, follow instrument manufacturer's recommendations for specific operating parameters. It is strongly recommended to use pyrolytically coated graphite tubes; these have significantly prolonged lifetime and enhance sensitivity about fivefold.

In case a calibration curve cannot be used because of the changing characteristics of the graphite tube, it is recommended that samples be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended would be as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, etc.

8.3.7 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

8.4.1 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.

8.4.2 Procedure for determining recovery. An aliquot of a standard solution containing 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 recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 25-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5x, 1X and 2X the OSHA ceiling standard) were spiked accordingly by adding an aliquot of a solution of vanadium pentoxide containing known amounts of vanadium. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 94.3%.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 From the standard V_2O_5 working standard solution, prepare at least six calibration standards to cover the V_2O_5 concentration range from 0.5 to 7 µg per 10 ml. Prepare these calibration standards fresh daily and make all dilutions with 0.01N NaOH. (Express concentration as µg V_2O_5 per 10 ml.

9.2 Proceed as in Section 8.3.7.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/10 ml. See special comments in 8.3.6. Special care must be given to proper calibration due to irregular behavior of some graphite tubes.

9.4 In cases where a calibration curve could not be used reliably, determine the appropriate response factor. To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 10 ml. Or alternatively, determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor determined from the response of the calibration standard. All data are expressed as V_2O_5.

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 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 = sample 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).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

11.1 Christian, Gary and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., 1970

11.2 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."

11.3 Vanadium, V_2O_5 Fume, S388 Backup Data Report prepared under NIOSH Contract No. 210-76-0123.

11.4 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1971.

11.5 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

Sampling Data Sheet No. S388

Substance

Vanadium, V_2O_5 Fume

Standard

Ceiling Value: 0.1 mg/cu m

Analytical Method

A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the vanadium oxide fume present. The sample filters are placed in 0.01N NaOH and the vanadium oxide is solubilized by heating at 50° C for 15 minutes. The quantity of analyte present is determined by flameless atomic absorption spectrophotometry at 318.4 nm, using a high temperature graphite atmomizer. The method has been validated over the concentration range of 0.06-0.29 mg/cu m for a 25-liter sample at 23°C and 761 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The following items are needed: a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at a flow rate of approximately 1.5 liters per minute, a 37-mm three-piece cassette filter holder held together by tape or shrinkable band, and a 37-mm/ 0.8 micrometer mixed cellulose ester membrane filter (MCEF) supported by a cellulose backup pad.

Sample Size

V_2O_5 fume has a ceiling value and therefore a maximum sampling period of 15 minutes is recommended. Sample at a flow rate of about 1.5 liters per minute for 15 minutes (22.5 liters).

Sampling Procedure

1. Assemble the filter and three-piece filter cassette and close firmly to insure that the center ring seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

2. Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3. Air being sampled should not be passed 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 all the necessary information to determine flow

rate of volume and record also the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. The pump rotameter should be observed frequently, and readjusted as needed. If the flow rate cannot be adjusted to correct a problem, terminate the sampling.

5. Collected sample cassettes should be firmly sealed with plugs in both the inlet and outlet.

6. Carefully record sample identity and all relevant sample data.

7. Blank. 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 method does not distinguish between V_2O_5 dust and fume.

Shipping Instructions

The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

Reference

Vanadium, V_2O_5 Fume, NIOSH Method No. S388.

Backup Data Report

Substance: Vanadium, V_2O_5 Fume, No. S388

OSHA Standard: 0.1 mg/cu m (Ceiling)

Chemical Used for Validation: Vanadium Pentoxide, V_2O_5, 100%, certified, Fisher Scientific Co.,
Ammonium metavanadate, NH_4VO_3, Ventron Corp.

General Considerations

The method for vanadium, V_2O_5 fume, 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 method should read to within $\pm$25% of the true value at the statistical confidence level of 95% over the range of 0.5 to 2X 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 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 the method for vanadium, V_2O_5 fume, consisted of the following experimental studies:

- Analysis of a set of 18 analytical samples (6 samples at each of three test levels) prepared by adding known aliquots of an alkaline solution of V_2O_5 to 37-mm Type AA Millipore filters, 0.8 micrometer pore size.

- Analysis of a set of 18 samples (6 samples at each of the three test levels) collected from dynamically generated test atmospheres to represent 15-minute samples (25-liters) at 0.5, 1 and 2X the acceptable ceiling concentration. The V_2O_5 fume was generated by thermal decomposition of ammonium metavanadate and collected samples have been analyzed by infrared spectroscopy to confirm conversion to V_2O_5.

- Determination of the collection efficiency of V_2O_5 fume on mixed cellulose ester membrane filter.

- Testing the storage stability of collected samples.

- Assessing the precision and accuracy of the method.

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

Principle of the Method

The method validated for the analysis of vanadium, V_2O_5 fume in air is based on collection on mixed cellulose ester membrane filter, recovery from the filter by base dissolution and analysis by flameless atomic absorption spectrophotometry using a high temperature graphite atomizer (HGA). The method is for vanadium oxides, but all data should be expressed as V_2O_5.

Analysis

A detailed description of the procedure for analysis, the preparation of analytical samples for the determination of sample recovery and the preparation of calibration standards are given in NIOSH Method No. S390 (Reference 3).

The reliability of the analytical method was tested, based on the analysis of 18 filter samples. The analytical samples were prepared by spiking 37-mm Type AA Millipore filters with known aliquots of a solution of V_2O_5 in 0.01 N sodium hydroxide. The aliquots added contained respectively 1.25, 2.50 and 5.00-micrograms of V_2O_5 fume.

The sample-containing filters were treated with 0.01 N NaOH and the analyte was dissolved by heating for 15 minutes in a water bath maintained at 50°C. Analyses were done with a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer equipped with a hollow cathode lamp for vanadium, a high temperature graphite atomizer and a deuterium arc background corrector. The absorbance, measured at 318.4 nm, was used as a measure of the vanadium concentration in the sample. Appropriate standard solutions, prepared from a 250 ppm V_2O_5 stock standard, were analyzed on the same day the samples were analyzed. The data for the full set of 18 analytical samples are shown in Table S388-1. The average analytical method recovery found was 94.3%; this factor was not used to correct the sampling and analysis data.

Sampling and Analysis

The basic equipment assembly used for the generation of V_2O_5 dust consists of the aerosol generator described in Attachment A with the aerosol generator part modified as described in Attachment B.

The precursor aerosol was produced by atomization of an aqueous solution of ammonium metavanadate. To produce the three test levels equivalent to the 0.5, 1 and 2X OSHA ceiling concentration, an aqueous solution containing 1.54 g ammonium metavanadate per liter was used.

The ammonium metavanadate aerosol was decomposed by passage through a quartz tube heated by two 1-foot tube furnaces in tandem and maintained at a temperature of 800 °C. It was found that thermal decomposition of ammonium metavanadate to vanadium pentoxide was virtually complete under these conditions. This observation is based on confirmatory qualitative assay of the collected particulate by infrared spectroscopy; there was no evidence of residual ammonium metavanadate and only V_2O_5 appeared

Table S388-1

Data Sheet: Vanadium, V_2O_5, Fume No. S388

Analysis*

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
1.25	1.24	0.992	2.50	2.34	0.936	5.00	3.80	0.760
1.25	1.01	0.808	2.50	2.25	0.900	5.00	4.60	0.920
1.25	1.21	0.968	2.50	2.42	0.968	5.00	4.63	0.926
1.25	1.16	0.928	2.50	2.37	0.948	5.00	4.75	0.950
1.25	1.42	1.136	2.50	2.36	0.944	5.00	4.66	0.932
1.25	1.24	0.992	2.50	2.42	0.968	5.00	5.00	1.000
n =		6			6			6
mean		0.971			0.944			0.915
std dev		0.1063			0.0252			0.0811
CV_1		0.1095			0.0267			0.0887

$\overline{CV_1}$ 0.0828

$\overline{CV_{A+\overline{AMR}}}$ 0.0894

* The samples were prepared using a solution of V_2O_5 in 0.01 NaOH. All data are expressed as V_2O_5.

to be present based on the IR spectra. Vanadium pentoxide and ammonium metavanadate reference standards were used to prepare authentic IR spectra.

Studies were also conducted to determine the particle size distribution of the vanadium fume aerosol produced in the test chamber.by sampling with an Andersen cascade impactor (Particle Fractionation Personnel Sampler) and determination of the amount of vanadium fume deposited at each stage by AAS. The data obtained by AAS analysis of the vanadium fume collected at each stage of the cascade impactor are tabulated below. The effective cut-off 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 liter per minute. The cumulative % is based on cumulating from the last stage of the impactor.

Stage	Particle Size Range Cut-off (micrometers)	µg V_2O_5 Found	% Total Particles	Cumulative %
1	4.7 and up	--	0.00	100.0
2	<4.7 - 3.3	0.12	0.54	100.0
3	<3.3 - 2.1	0.17	0.77	99.46
4	<2.1 - 0.65	4.18	18.87	98.69
Backup Filter	<0.65	17.68	79.81	79.82
	Total	22.15		

A set of 18 generated/collected samples (6 samples at each of the three test levels) were analyzed. The data for these samples are shown in Table S388-2.

Storage Stability

Studies were done to assess the stability of V_2O_5 fume samples upon storage for one week at atmospheric conditions. For these studies, six generated/collected samples were analyzed after overnight storage and the results were compared with similar data obtained for six generated collected samples stored for seven days. These 12 samples were collected simultaneously. The data for these samples given in Table S388-3 show that the samples are stable over a seven-day period; the average value found was 0.1402 mg/cu m for the one-day-old samples vs 0.1468 mg/cu m for the seven-day-old samples.

Collection Efficiency

The collection efficiency of the 37-mm Type AA Millipore filter for V_2O_5 fume was determined by collecting six filter samples at an air sample concentration of 0.294 mg/cu m for a 25-liter sample. The physical lay-out of the filter series (front and backup) used for all the samples was such that the two filters were physically separated from each other and only the backup filter was supported by a backup pad. The overall

Table S388-2

Data Sheet: Vanadium, V_2O_5, Fume, No. S388

Sampling and Analysis

Test Level	Found		
	µg V_2O_5	Liters	mg/cu m
0.5S	1.31	22.82	0.0574
	1.38	22.75	0.0607
	1.35	22.66	0.0596
	1.37	22.79	0.0601
	0.76	22.72	0.0335*
	1.42	22.31	0.0636
		n = 5	
		mean	0.0603
		std dev	0.00224
		CV_2	0.0371
1S	3.12	22.85	0.1365
	3.15	22.88	0.1377
	3.08	22.76	0.1353
	3.17	23.08	0.1373
	3.08	23.18	0.1329
	1.23	23.05	0.0534*
		n = 5	
		mean	0.1359
		std dev	0.00193
		CV_2	0.0142
2S	6.51	22.85	0.285
	6.65	22.82	0.291
	7.13	22.84	0.312
	6.67	22.82	0.292
	6.67	22.78	0.293
	6.92	23.81	0.291
		n = 6	
		mean	0.294
		std dev	0.00925
		CV_2	0.0315

$\overline{CV}_2$ = 0.0293

* These values were excluded from statistical analysis based on Grubb's test.

Table S388-3

Stability of Generated/Collected V_2O_5 Dust Samples

Samples Stored 1 Day			Samples Stored 7 Days		
µg found	Liters	mg/cu m	µg found	Liters	mg/cu m
2.72	22.86	0.1190	3.34	23.01	0.1452
3.30	22.89	0.1442	3.20	23.04	0.1389
3.31	22.77	0.1454	1.56	22.92	0.0681*
3.28	23.10	0.1420	3.51	22.95	0.1529
3.33	23.21	0.1435	3.26	23.05	0.1414
3.39	23.07	0.1469	3.57	22.92	0.1558
	n = 6			n = 5	
	mean	0.1402		mean	0.1468
	std dev	0.0105		std dev	0.00726
	CV	0.0750		CV	0.0496

* This data is excluded from statistical analysis based on Grubb's test.

average collection efficiency found was 100% (or at least 97.8%) at the 2S test concentration studied as indicated by the data summarized in Table S388-4.

Independent Method of Verifying Generator Concentration

A separate set of experiments was conducted to support the accuracy of the data for the set of 18 generated/collected samples, i.e., the amount found is the best estimate of generator concentration based on collection efficiency, analytical method recovery, and sample stability data.

For this supporting study, a set of 12 samples was collected simultaneously for 15 minutes using the 14-port sampling manifold at the 1S test level. A separate set of 6 samples was also collected for a total period of 120 minutes at the 1S sampling manifold. The experiment was planned such that the 15-minute samples were collected midstream of the 120-minute samples (i.e., 120-minute sampling was broken up into 60 minutes first, interrupted to collect the separate set of twelve 15-minute samples, and then continued for another 60 minutes using the original six filters). This procedure was adapted to minimize the effect of any change in the generator concentration during the interval.

The samples were split into two sets of three 120-minute samples (180 liters) and six 15-minute samples (25 liters) and one set (Set A) was analyzed by AAS/HGA as described and the other set (Set B) was analyzed by X-ray fluorescence. The X-ray fluorescence studies were attempted in order to obtain a truly independent measure of the V_2O_5 concentration. The X-ray fluorescence analysis was done based on the use of calibration data obtained from V_2O_5 standards prepared by adding known amounts of V_2O_5 to 13 mm mixed cellulose ester membrane filter. Intensity measurements were done at the first order reflection for vanadium K_α using a Philips Electronic Instrument X-ray spectrometer. Appropriate corrections were made to account for the size of the filter containing the V_2O_5 standards (13 mm), the unknown sample (37-mm), and the "illumination" area of the X-ray beam which was controlled by the use of a thin lead disc with a diameter of 11.8 mm. While the results obtained from this study are promising as an analytical technique and consistent with the AAS data, the XRF method would need much more study of calibration details before it could be used as a truly independent measure of concentration.

The data for these samples are summarized in Table S388-5. Note that only three 15-minute samples and the three 120-minute samples were analyzed by X-ray fluorescence.

The data obtained by AAS/HGA analysis show good agreement between the found and taken generator concentrations, 93.2%. In addition, the found concentration is supported by the data from the samples analyzed by X-ray fluorescence.

Table S388-4

Collection Efficiency of V_2O_5 Fume on Type AA Millipore Filters

Sample size: 25 liters at 0.294 mg/cu m*

----------µg Found----------			
Front	Backup	Total	% Collected in Front
6.51	N.D.	6.51	100
6.65	N.D.	6.65	100
7.13	N.D.	7.13	100
6.67	N.D.	6.67	100
6.67	N.D.	6.67	100
6.92	N.D.	6.92	100

Average Collection Efficiency 100**

N.D. = Not detectable; the detection limit was 0.10 µg V_2O_5 in a total solution volume of 10 ml.

* The test concentration noted is based on the average concentration found for the six samples at the 2S test level (See Table S388-2).

** The minimum average collection efficiency can also be expressed as 98.5% on the basis of the detection limit and the average µg found on the front filter.

Table S388-5

Independent Method of Verifying Generator Concentration

A. Samples Analyzed by AAS/HGA

--Taken Concentration--- 120-minute Samples			--Found Concentrations-- 15-minute Samples		
µg	Liters	mg/cu m	µg	Liters	mg/cu m
32.6	180.8	0.1803	4.21	22.60	0.1863
37.3	180.2	0.2070	3.55	22.53	0.1576*
38.1	179.0	0.2128	4.29	22.38	0.1917
			4.22	22.60	0.1867
			4.25	22.60	0.1881
			4.03	22.47	0.1794
	n = 3			n = 5	
	mean	0.2000		mean	0.1864
	CV	0.0867		CV	0.0240

B. Samples Analyzed by X-ray Fluorescence

---------- Taken Concentration ---------- 120-minute Samples			15-minute Samples		
µg	Liters	mg/cu m	µg	Liters	mg/cu m
36.9	180.8	0.2041	3.65	22.53	0.1620
28.9**	180.8	--	3.52	21.26	0.1656
37.2	179.6	0.2071	3.67	22.19	0.1654
	n = 2			n = 3	
	mean	0.2056		mean	0.1643
	CV	0.0103		CV	0.0123

* This value was rejected based on Grubb's Outlier Test

** This sample was smeared indicative of leakage during sampling

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and summarized in Attachment C, and the data in Tables S388-1 and S388-2.

Bartlett's test for homogeneity of coefficients of variation at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for vanadium oxides fume. The data (Table S388-2) gave a chi square value of 2.96; indicating that the hypothesis of equal coefficients of variation 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:

$$\overline{CV}_1 = 0.0828 \qquad \overline{CV}_2 = 0.0294 \qquad \overline{CV}_T = 0.0671$$

The experimentally determined $\overline{CV}_T$ value is a good estimate not only of the precision but also of the accuracy of the method. This assumption is supported by the data for a set of samples representing the 1S test level as described in the section on Independent Method. For these samples, the taken concentration is represented by the data from the 120-minute samples analyzed by AAS/HGA. The agreement found by the trial X-ray fluorescence method was also compared with the AAS data. The agreement between the found and taken concentrations using these approaches is summarized below.

Analysis Method for Taken Value	mg/cu m		% Agreement (Found ÷ Taken)
	Average Taken*	Average Found	
AAS/HGA	0.2000	0.1864	93.2
X-ray Fluorescence	0.2056	0.1864	90.7

*120-minute samples.

The difference between the taken and found concentrations (AAS data taken as primary reference point) 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 and storage stability test described in the appropriate sections. Moreover, the vapor pressure of V_2O_5 at 25°C is 1.46×10^{-21} atm and thus no V_2O_5 could have been lost in the vapor phase.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, U.S. Government.

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. Vanadium, V_2O_5 Fume, NIOSH Method No. S388, prepared under NIOSH Contract No. 210-76-0123, with validation date 1/21/77.

ATTACHMENT A

AEROSOL GENERATION/DILUTION/SAMPLING SYSTEM

The aerosol dilution and sampling system is shown schematically in Figure 1. Basically the system consists of a main horizontal line into which aerosol and dilution air are introduced and three vertical dilution and sampling sections which branch off the main line. Figure 2 shows the latter sections in more detail.

Aerosol dilution ratios in the system are fixed by the action of critical flow orifices. Usually an aerosol with a concentration twice the OSHA standard is prepared in the mainline, and this aerosol sampled without dilution in one dilution/sampling section and diluted twofold and fourfold in the other two sections. Other dilution modes may be accommodated simply by changing the critical orifices. The system is shown in Figure 1 as it would be used for collecting six samples at each concentration level. A fourteen port sampler is also available for use when additional samples are required.

There is a luer fitting on each sample port to mate with a Millipore filter cassette. Sampling flowrates are controlled by critical orifices located on each sample manifold.

A number of different aerosol generators including a pneumatic atomizer, an ultrasonic nebulizer, and a dust disperser may be used in conjunction with the dilution and sampling system.

Aerosol Generation

The following aerosol generation equipment is available for use with the system:

- Environmental Research Corporation Fluid Atomization Aerosol Generator Model 7330
- DeVilbiss Model 35A Ultrasonic Nebulizer
- Royco Model WA Aerosol Generator
- Wright Dust Feeder

The ERC and DeVilbiss generators are used to produce aerosols by spray drying or by atomization of suspended solid particles. For spray drying, the material to be dispersed is dissolved in an appropriate solvent, the solution atomized, and the resulting mist mixed with solvent-free air. The solvent evaporates and leaves the nonvolatile solute behind as a residue. Either solid or liquid solutes may be used. Aerosols with median diameters in the 0.03 to 0.5 micron particle size range may be prepared by spray drying with the ERC atomizer. Slightly larger particles may be prepared by spray drying from the DeVilbiss unit. Both aerosol concentration and particle size are functions of the concentration of solute in the atomized solution.

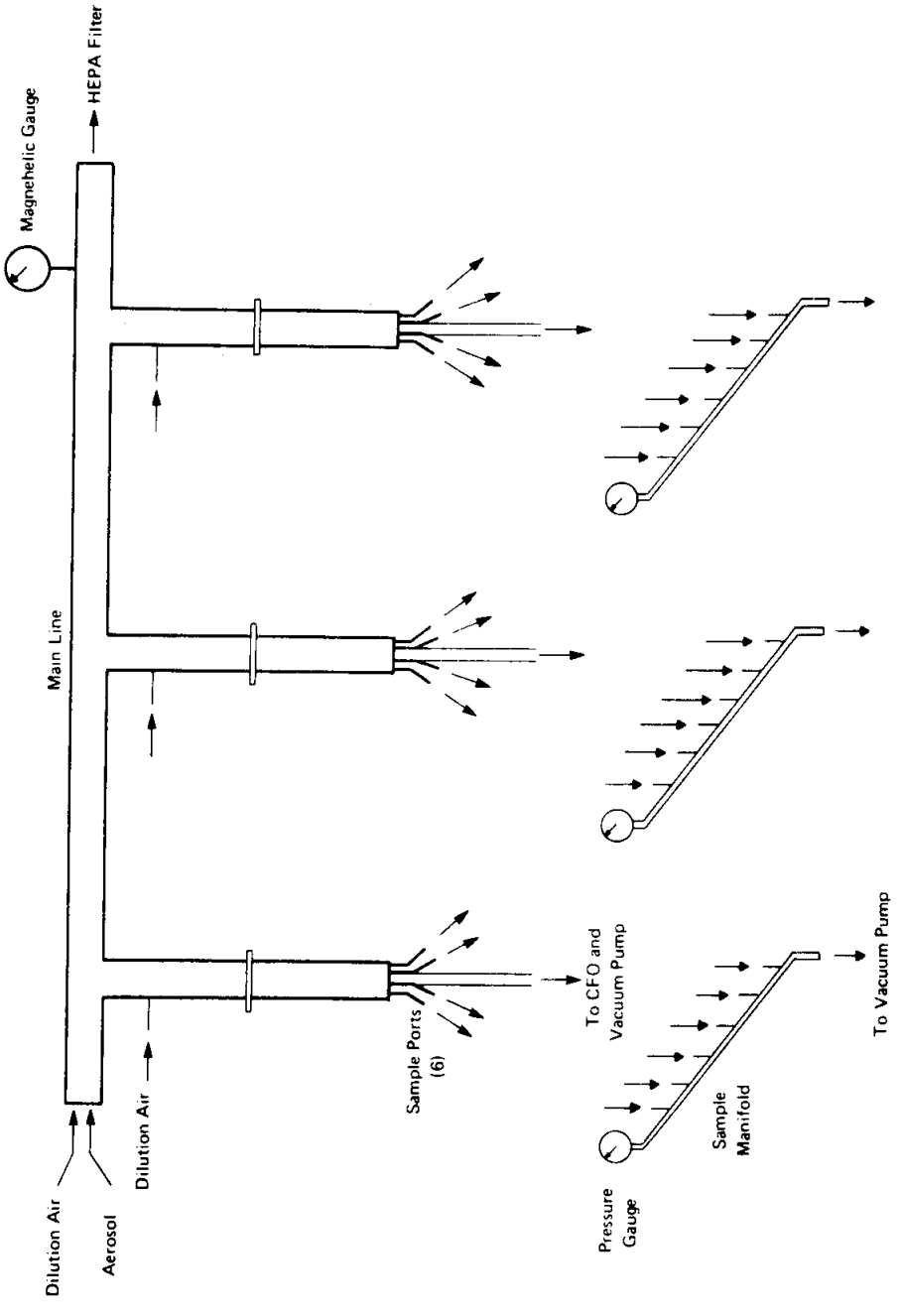
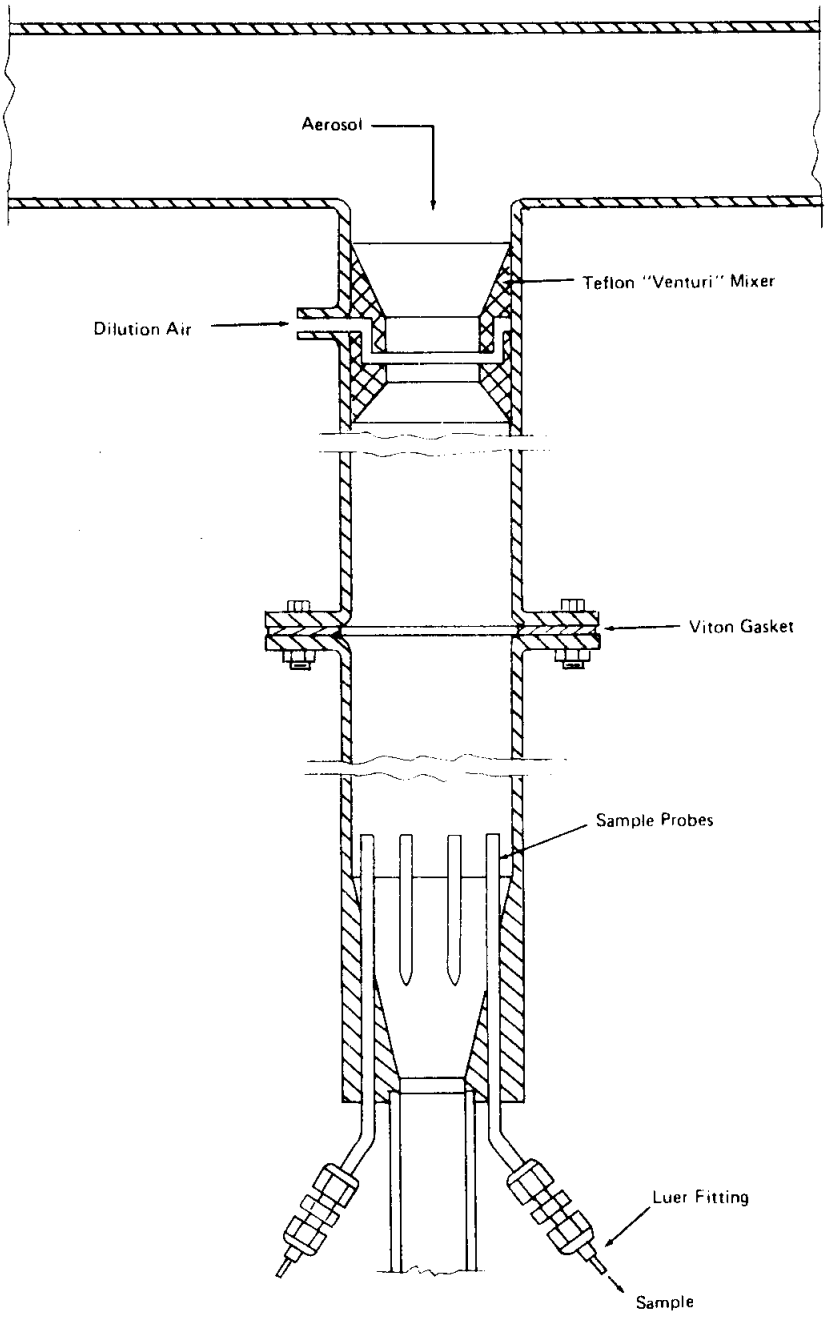


Figure S388-A-1 Aerosol Dilution and Sampling System



CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION

Figure S388-A-2

Aerosols of solid particles may also be prepared by suspending the particles in a solvent, atomizing the solution and vaporizing the solvent. Solid suspensions with particles up to several microns in diameter may be dispersed with the ERC and DeVilbiss atomizers.

The Royco generator is used primarily to atomize pure liquids. It was designed specifically for atomizing organic liquids such as dioctyl phthalate, and produces DOP aerosol with a median diameter of between 0.5 and 1.0 micron.

The Wright Dust Feeder is used to disperse powders. Samples to be dispersed in the apparatus are compressed into a special holder. In operation, the holder and the dust compact are slowly rotated and driven against a stationary scraper blade which continuously removes dust from the compact surface at a uniform rate. The rate of dust delivery from the feeder may be varied by changing gears in the compact advance mechanism. The powder is entrained in an air stream and is dispersed by impaction on a metal plate. Ideally the size distribution of the particles in the dust cloud should be governed by the particle size distribution of the original powder, however, in practice it is usually difficult to disperse a powder completely. Agglomerates are often formed.

Air Supply

Air from the house compressed air system is treated by successive passage through a cotton filter, a silica gel bed, a high efficiency glass fiber filter, and a membrane filter. These remove respectively, oil and water droplets, water vapor, and fine particles.

The treated air then passes to two parallel air supply manifolds, each of which is equipped with valves for controlling air flow to various parts of the generation/dilution system. One of the manifolds supplies air to the dilution system. The second supplies air to the aerosol generator, either directly or through calibrated rotameters as may be required by the particular generator being used. Pressure in each manifold is maintained at a fixed level by Moore Nullmatic pressure regulators and is measured with bourdon gauges (6" Ashcroft test gauges).

Dilution and Sampling Sections

Aerosol dilution occurs in the Teflon venturi-shaped inserts shown in Figure 2. Dilution air is injected radially into the venturi throat. The quantity of dilution air introduced is fixed by a critical orifice which is connected to one of the constant pressure air manifolds.

Isokinetic sampling probes are located approximately thirty centimeters downstream of each diluter. The probes convey aerosol to sample collectors (filter cassettes) mounted radially around the outside

of the sampling section. Sample flowrate is fixed at 1.5 liters per minute by critical orifices (sapphire orifices supplied by Richard H. Bird and Co., Waltham, Mass.) mounted on the sample manifold (Figure 1).

As is indicated in Figure 1, aerosol which does not pass through the sample ports exits from each dilution/sampling section through a large critical orifice. The flow rate through this orifice is about 60 liters per minute. The orifice is protected from contamination by a high efficiency filter.

The dilution ratio in each section is given by:

$$\frac{Q_A}{Q_A + Q_D}$$

where Q_A is the flowrate of aerosol entering the section from the mainline and Q_D is the dilution air flowrate. Letting Q_S be the total sample flowrate and Q_T be the flow through the large ($\sim$60 lpm) orifice, and using the fact that $Q_T + Q_S = Q_D + Q_A$ (assuming uniform pressure and temperature in the section), the dilution ratio may be rewritten as:

$$R = \frac{Q_T + Q_S - Q_D}{Q_T + Q_S}$$

Since Q_T, Q_S, and Q_D are controlled by the action of critical orifices, the dilution ratio is also fixed by the flowrate through the orifices.

Dilution ratios are measured by adding a small quantity of hydrocarbon gas to the main line and measuring the relative concentrations in each of the three sampling sections using a Beckman 402 hydrocarbon analyzer. Dilution ratios of 1.00 to 0.488 to 0.241 are typical when the system is set to generate a 2X OSHA standard concentration in the main line. No measurable differences (within 1%) in the hydrocarbon concentration were found among the six sample ports on any of the three sampling ports. The dilution ratios are rechecked periodically.

The main line flowrate is about 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.

Experimental Procedure

1) The aerosol generator parameters necessary to produce the desired aerosol concentration are found by making several trial runs. If the spray drying procedure is being used, the concentration of the atomizer solution would be varied in the trial runs. If the dust feeder were being used, the sample feed rate would be varied.

2) Six samples, each consisting of two filters sampling in series are taken from the 2X OSHA standard sampling ports to verify that the collection efficiency of the filters is adequate.

3) A full set of eighteen (or twenty-six) samples can be collected simultaneously.

Typical System Parameters

When the dilution/sampling system is set up to produce aerosols with a 2X OSHA standard concentration in the main line, typical values of the system parameters are:

Main line pressure:	+ 3 cm H_2O with respect to atmospheric pressure
Main line flowrate:	130 liters per minute
Sampling rate:	1.5 liters per minute
Flowrate through dilution/ sampling branch (approximate):	68 liters per minute

Dilution air flowrate (approximate):

2X OSHA standard branch	0
1X OSHA standard branch	36
0.5X OSHA standard branch	53

Dilution ratios (measured with hydrocarbon analyzer):	1.00:0.488:0.241

Attachment B

FUME GENERATION

The fume generator produces submicron metal oxide aerosols by generating an aerosol of a metal compound which may be thermally decomposed to yield the oxide.

Precursor aerosols are prepared by spray-drying an aqueous solution of a metal compound. This is done with an Environmental Research Corporation Fluid Atomization Aerosol Generator. The ERC generator is basically a Collison atomizer with facilities for adding dilution air to the atomizer output. It also has a one millicurie Krypton-85 charge neutralizer.

The precursor aerosol is decomposed by passage through a quartz tube heated by two tube furnaces. The heated section of tubing is about sixty-six centimeters in length and one-and-one half centimeters in interior diameter. Aerosol flows through the tubing at about ten liters per minute. The heated section of tubing is enclosed in a stainless steel tube to promote even heating.

The oxide aerosol is cooled by passage through a short water jacketed condenser and is then diluted about ten-fold with dry filtered room temperature air. Dilution serves to further cool the aerosol and to provide the proper final flow rate and concentration.

Metal compounds are chosen as oxide precursors on the basis of its solubility in water and the ease with which it can be thermally decomposed. Typically, the solubility requirement can be gauged on the experimentally documented estimate that a solution concentration of about 12 grams of metal per liter of solution will produce an aerosol metal concentration of 2 mg/cu m at the 2S sampling lines.

The mass median diameter of the aerosol generated with a Collison atomizer is about two microns.* Consequently an aerosol produced by spray-drying solution droplets from this atomizer would have a mass median diameter of approximately $2(C)^{1/3}$ microns, where C is the volume of solute per unit volume of solution. This assumes that the dry particles are spheres and that the presence of the solute does not affect the atomization.

* May, K.R., Aerosol Sci 4, 235 (1973).

Attachment C

SUMMARY OF STATISTICAL TERMS AND FORMULAE

The statistical analysis employed in this program has been provided by NIOSH. The evaluation of the limits and guidelines are discussed in a series of memoranda from Busch (Reference A). Some key terms, statistical formula, acceptable limits and statistical tests which have been used in these reports are noted and summarized herein.

Mean - Arithmetic mean or average, defined as the sum of all the observations divided by the number of observations (n).

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

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

CV - Coefficient of Variation or Relative Standard Deviation, defined as the standard deviation divided by the mean.

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

CV_1 - Coefficient of Variation for the six analytical samples at each of the 0.5, 1, and 2X OSHA standard level.

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

$\overline{CV}$ - Pooled Coefficient of Variation; in this program, the value is derived from the coefficients of variation obtained from the analysis of 6 samples at each of the three test levels - 0.5, 1 and 2X OSHA standard level. The mathematical equation is expressed as:

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

where:

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

CV_i = Coefficient of Variation of the observations at the i^{th} level

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

$\overline{CV}_1$ - Pooled Coefficient of Variation calculated as above based on data for the 18 analytical samples

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

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

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

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

$\overline{CV}_2$ - Pooled Coefficient of Variation based on the data for the 18 generated samples.

$\overline{CV}_S$ - Coefficient of Variation of the sample collection, the value is dependent on the data from the 18 analytical and 18 generated samples.

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

$\overline{CV}_P$ - Coefficient of Variation due to the pump error, assumed to be equal to 0.05.

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

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

or:

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

Grubb's Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

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

where:

x = observation being tested

$\bar{x}$ = mean of all observations

s = standard deviation based on n degrees of freedom.

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

Bartlett's Test for Homogeneity of 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:

$$\text{Chi Squared} = \frac{f \ln \left(\overline{CV_2}\right)^2 - \sum_{i=1}^{n} f_i \ln \left(\overline{CV}_{2i}\right)^2}{1 + \frac{1}{3(k-1)} \left[\left(\sum_{i=1}^{n} \frac{1}{f_i}\right) - \frac{1}{f}\right]}$$

where:

$\overline{CV_2}$ = Pooled Coefficient of Variation of 18 generated samples.

$\overline{CV}_{2i}$ = Coefficient of Variation of 6 generated samples at the i^{th} level.

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

i = 1, 2, 3..... n

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

k = number of variances being tested; in this program k = 3.

In order to pass Bartlett's test at the 1% significance level, chi squared must be less than or equal to 9.21 when k = 3.

Reference

A. Kenneth A. Busch Memoranda to Deputy Director, DLCD, on the subject "Statistical Protocol for Analysis of Data from Contract No. CDC-99-74-45", dated 1/16/75, 11/8/74.