



NIOSH Analytical Methods for Set L

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 is 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. These methods have been validated and are suitable for measuring airborne concentrations of these substances 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 L

Acetic Anhydride	Acetonitrile
Cresol, all isomers	Dimethyl Aniline✓
Hydrogen Bromide	Hydrogen Fluoride
Phenol	Phenylhydrazine✓
Pyridine	Sulfuric Acid
o-Toluidine	Xylidine

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
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16. Abstracts Industrial Hygiene sampling and analytical monitoring methods validated under the joint NIOSH/OSHA Standards Completion Program for Set L are contained herein. Monitoring methods for the following compounds are included: <table border="0"> <tr> <td>Acetic Anhydride</td> <td>Acetonitrile</td> </tr> <tr> <td>Cresol, all isomers</td> <td>Dimethyl aniline</td> </tr> <tr> <td>Hydrogen Bromide</td> <td>Hydrogen Fluoride</td> </tr> <tr> <td>Phenol</td> <td>Phenylhydrazine</td> </tr> <tr> <td>Pyridine</td> <td>Sulfuric Acid</td> </tr> <tr> <td>o-Toluidine</td> <td>Xylidine</td> </tr> </table>						Acetic Anhydride	Acetonitrile	Cresol, all isomers	Dimethyl aniline	Hydrogen Bromide	Hydrogen Fluoride	Phenol	Phenylhydrazine	Pyridine	Sulfuric Acid	o-Toluidine	Xylidine
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17. Key Words and Document Analysis. 17a. Descriptors Chemical analysis Sampling <table border="0"> <tr> <td>*Acetic Anhydride</td> <td>*Acetonitrile</td> </tr> <tr> <td>*Cresol, all isomers</td> <td>*Dimethyl aniline</td> </tr> <tr> <td>*Hydrogen Bromide</td> <td>*Hydrogen Fluoride</td> </tr> <tr> <td>*Phenol</td> <td>*Phenylhydrazine</td> </tr> <tr> <td>*Pyridine</td> <td>*Sulfuric Acid</td> </tr> <tr> <td>*o-Toluidine</td> <td>*Xylidine</td> </tr> </table>						*Acetic Anhydride	*Acetonitrile	*Cresol, all isomers	*Dimethyl aniline	*Hydrogen Bromide	*Hydrogen Fluoride	*Phenol	*Phenylhydrazine	*Pyridine	*Sulfuric Acid	*o-Toluidine	*Xylidine
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Acetic Anhydride

Analyte:	Acetic Anhydride	Method No.: S170
Matrix:	Air	Range: 9.35-37.4 mg/cu m
OSHA Standard:	5 ppm (20 mg/cu m)	Precision ($\overline{CV}_T$): 0.060
Procedure:	Bubbler collection, colorimetric	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 Acetic anhydride is collected in a standard midget bubbler charged with an alkaline solution containing hydroxylamine.
- 1.2 The resulting product is reacted with ferric chloride to form a purple complex.
- 1.3 The absorption maximum at 540 nm is used to measure the acetic anhydride reaction product.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 9.35-37.4 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg. The probable useful range of the method is 5-45 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where the absorbance is greater than the limits of the standard curve, the samples can be diluted with the collection medium prior to color development to extend the upper limit of the range.
- 2.2 A concentration of 5 mg/cu m of acetic anhydride can be determined in a 100-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 1-cm cell. Greater sensitivity could be obtained by use of a longer path length cell.

3. Interferences

- 3.1 Any material containing an organic carbonyl group will interfere. Among such materials are esters, acid chlorides, and aldehydes.
- 3.2 A potential interfering substance that is most likely to coexist with acetic anhydride in air is ketene.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 9.35-37.4 mg/cu m was 0.060. This value corresponds to a 1.2 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 Reference 11.2.
- 4.2 A collection efficiency of 1.00 ± 0.01 was determined for the collection medium; thus no bias was introduced in the sample collection step. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.5% higher 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 in paragraph 10.3.

5. Advantages and Disadvantages of the Method

- 5.1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.
- 5.2 The alkaline solution containing hydroxylamine can produce dermatitis if it comes in contact with the skin.
- 5.3 The method is simple and requires approximately 1.5 hours to complete.

6. Apparatus

- 6.1 Sampling Equipment. The sampling equipment for the bubbler collection method consists of the following components:
 - 6.1.1 A glass standard midget bubbler with stem which has a fritted glass end and containing the absorbing solution (Section 7.4). The fritted end should have porosity approximately equal to that of Corning EC (170-220 μ maximum pore diameter).

- 6.1.2 A pump suitable for delivering at least 1 liter per minute for 100 minutes. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.
- 6.1.3 An integrating volume meter such as a dry gas meter or wet test meter.
- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.
- 6.2 A spectrophotometer capable of measuring the developed color at 540 nm.
- 6.3 Matched glass cells or cuvettes, 1-cm path length.
- 6.4 Assorted laboratory glassware--pipets, volumetric flask, and graduated cylinders of appropriate capacities.
- 7. Reagents
 - All reagents must be ACS reagent grade or better.
 - 7.1 Distilled water.
 - 7.2 Hydroxylamine hydrochloride solution. Prepare this solution by dissolving 200 g in distilled water in a 1-liter volumetric flask. Dilute to mark with distilled water and transfer the solution to a light protected container. Store the solution in a refrigerator and reject any solution when it is two weeks old.
 - 7.3 Sodium hydroxide solution. Prepare this solution by dissolving 200 g in distilled water in a 1-liter volumetric flask. Cool the solution to room temperature and dilute to volume.
 - 7.4 Absorbing solution. Mix equal volumes of the hydroxylamine hydrochloride and sodium hydroxide solution. This mixture is stable for only two hours and should be prepared fresh just prior to use.
 - 7.5 Ferric chloride solution. Dissolve 100 g of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in a 1-liter volumetric flask in a mixture of equal volumes of water and concentrated hydrochloric acid. Make to volume.
 - 7.6 Acetic anhydride standard solution. Pipet 10 ml of acetic anhydride into a 100-ml volumetric flask and make to volume with acetone. The solution must be prepared within two hours of use.

8. Procedure

- 8.1 Cleaning of equipment. No specialized cleaning of glassware is required. However, since known interferences occur with esters and aldehydes, cleaning techniques should insure the absence of all organic materials.
- 8.2 Calibration of personal sampling pump. The pump should be calibrated using an integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Pour 10 ml of the absorbing solution (Section 7.4) into each bubbler.
 - 8.3.2 Connect the bubbler with a 5-cm glass adsorption tube (6-mm I.D. and 8-mm O.D.) containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.
 - 8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, the time and/or volume as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute. A sample size of 100 liters is recommended.
 - 8.3.4 After sampling, the bubbler stem can be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1-2 ml of the absorbing solution and add the wash to the bubbler. Then seal the bubbler with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
 - 8.3.5 Care should be taken to minimize spillage or loss by evaporation at all times.
 - 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
 - 8.3.7 A "blank" bubbler should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Transfer the solution to a 50-ml volumetric flask.
- 8.4.3 Rinse the bubbler twice with 1 ml of distilled water and add the rinses to the volumetric flask.
- 8.4.4 Pipet 5 ml of the ferric chloride solution into the volumetric flask.
- 8.4.5 Dilute to the mark with a solution containing equal volumes of sodium hydroxide solution, hydroxylamine hydrochloride solution, and ferric chloride solution. This solution should be made in an ice bath. The purple complex is formed rapidly.
- 8.4.6 Read the absorbance at 540 nm in the spectrophotometer against a blank prepared from the alkaline hydroxylamine solution and ferric chloride in the same fashion as the samples.

9. Calibration and Standards

9.1 Preparation of the Calibration Curve.

- 9.1.1 Pipet 10 ml of the absorbing solution into six 50-ml volumetric flasks.
- 9.1.2 Carefully transfer 0 (blank), 10, 20, 40, 80, and 100 microliters of the standard solution into the flasks (Section 7.6).
- 9.1.3 Add to this mixture 5 ml of ferric chloride solution (Section 7.5) using a 5-ml pipet.
- 9.1.4 Continue as described in Section 8.4.5.
- 9.1.5 Adjust the baseline of the spectrophotometer to zero with distilled water in both cells.
- 9.1.6 Measure the absorbance of the blank and standards at 540 nm.
- 9.1.7 Construct a calibration curve by plotting absorbance against equivalent milligrams of acetic anhydride.

10. Calculations

10.1 Subtract the absorbance of the blank from the absorbance of each sample.

10.2 Determine from the calibration curve (Section 9.1.7) the mg of acetic anhydride present in each sample.

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg acetic anhydride (Section 10.2)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 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 analyte

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 Diggle, W. M. and Gage, J. C., "The Determination of Ketene and Acetic Anhydride in the Atmosphere," Analyst, 78, 473 (1953).

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

Acetonitrile

Analyte:	Acetonitrile	Method No.: S165
Matrix:	Air	Range: 31.4-140.2 mg/cu m
OSHA Standard:	40 ppm (70 mg/cu m)	Precision ($\overline{CV}_T$): 0.072
Procedure:	Adsorption on charcoal, desorption with benzene, GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a large charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with benzene.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 31.4-140.2 mg/cu m at an atmospheric temperature and pressure of 22°C and 762 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 10-210 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of acetonitrile and other substances in the air. The first section of the charcoal tube was found to hold 5.2 mg of acetonitrile when a test atmosphere containing 140 mg/cu m of acetonitrile in air was sampled at 0.196 liter

per minute for 190 minutes; breakthrough was observed at this time, i.e. the concentration of acetonitrile in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since benzene is used rather than carbon disulfide to desorb acetonitrile from the charcoal, it would not be possible to measure benzene in the sample with this desorbing solvent. If it is suspected that benzene is present, a separate sample should be collected for benzene analysis.
- 3.3 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 proof of chemical identity.
- 3.4 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 31.4-140.2 mg/cu m was 0.072. This value corresponds to a 5.0 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 Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.3% higher 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 in paragraph 10.5.

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 tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 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 the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, 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 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 9 cm long with a 8-mm O.D. and a 6-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 400 mg of charcoal, the backup section 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 one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Volumetric flasks: 10-ml or convenient sizes for making standard solutions and for desorbing the samples. If an automatic sample injector is used, aliquots of the samples may be transferred to the associated vials.

6.7 Microliter syringes: 10-microliter for injection of samples into the gas chromatograph.

6.8 Pipets: 5-ml delivery pipets.

7. Reagents

7.1 Chromatographic quality benzene.

7.2 Acetonitrile, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

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 charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube.

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. 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 charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 10-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 5 ml of benzene is pipetted into each sample container. (All work with benzene should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, transfer an appropriate amount of the sample to the automatic sample injector vials after desorption is complete. The sample vials should be capped as soon as the sample is added to minimize volatilization.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 270°C injector temperature

5. 285°C manifold temperature (detector)

6. 180°C column temperature

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 distillation 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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (400 mg) is measured into a 9 cm 6-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm.

A known amount of acetonitrile in benzene containing 157 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. 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 compound into 5.0 ml of benzene contained in a 10 ml volumetric flask. 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 analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/5 ml benzene, because samples are desorbed in this amount of benzene. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/5.0 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 known day-to-day variations and variations during the same day of the FID response.

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/5.0 ml benzene and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 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 analyte
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 No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Cresol, All Isomers

Analyte:	Cresol, all isomers	Method No.: S167
Matrix:	Air	Range: 10.54-42.2 mg/cu m
OSHA Standard:	5 ppm (22 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.068
Procedure:	Adsorption on silica gel, desorption with acetone, GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.
- 1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with acetone.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The combined areas of the resulting two peaks are determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 10.54-42.2 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-mg sample. The 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 silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 1.87 mg of analyte when a test atmosphere containing

42.2 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

- 3.1 Silica gel has a high affinity for water, so organic vapors will not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.
- 3.2 When compounds other than the isomers of cresol are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since acetone is used to desorb the analyte from the silica gel, it is not possible to measure acetone in the sample.
- 3.3 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 proof of chemical identity.
- 3.4 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 10.54-42.2 mg/cu m was 0.068. This value corresponds to a 1.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 4.2% 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 from paragraph 10.5.

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 tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 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 the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, 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 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 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 one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality acetone.

7.2 Cresol (all isomers) - prepare a standard mixture of the isomers by adding together 20 g of the ortho, 40 g of the meta, and 30 g of the para isomers and mix.

7.3 Prepurified hydrogen.

7.4 Filtered compressed air.

7.5 Purified nitrogen.

7.6 n-Hexane, reagent grade.

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 silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

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

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

8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. 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 silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool and the silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 230°C injector temperature
 - 5. 250°C manifold temperature (detector)
 - 6. 200°C column temperature

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 distillation 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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. Although there are three isomers of cresol, there are only two peaks on the gas chromatogram, because the meta and para isomers have the same retention time. The total area of the two sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm.

A standard solution is prepared by placing 1100 mg of the mixture of the isomers of cresol in a 10-ml volumetric flask and making it up to volume with n-hexane. A known amount of the standard solution is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. 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 the analyte onto the silica gel. 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 compound 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.) is dependent on the amount of analyte collected on the silica gel. The desorption efficiency 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 analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml acetone, because samples are desorbed in this amount of acetone. A series of standards, varying in concentration over the range of interest, are 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 total 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 known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each combined 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.

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

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 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 analyte
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 No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Dimethylaniline

Analyte:	Dimethylaniline	Method No.: S164
Matrix:	Air	Range: 10.5-46.7 mg/cu m
OSHA Standard:	5 ppm (25 mg/cu m)	Precision (CV_T): 0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 10.5-46.7 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 2.5-75 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1.5-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of dimethylaniline and other substances in the air. The first section of the charcoal tube was found to hold at least 2.1 mg of dimethylaniline when a test atmosphere

containing 47 mg/cu m of dimethylaniline in air was sampled at 0.186 liter per minute for 240 minutes; at that time the concentration of dimethylaniline in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 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.
- 3.3 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 proof of chemical identity.
- 3.4 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 (CV_T) for the analytical and sampling method at 1X the OSHA standard level in the range of 10.5-46.7 mg/cu m was 0.052. This value corresponds to a 1.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 8.6% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in paragraph 10.5.

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 tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 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 the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, 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 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 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 one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Dimethylaniline, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

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 charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least +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 charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 210°C injector temperature
 - 5. 260°C manifold temperature (detector)
 - 6. 200°C column temperature
- 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 distillation

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.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of dimethylaniline containing 312.5 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. 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 compound into 1.0 ml of carbon disulfide 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 analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 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 known day-to-day variations and variations during the same day of the FID response.

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 carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 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 analyte
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 No. CDC-99-74-45.

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

Hydrogen Bromide

Analyte:	Hydrogen Bromide	Method No.:	S175
Matrix:	Air	Range:	6.14-20.37 mg/cu m
OSHA Standard:	3 ppm (10 mg/cu m)	Precision ($\overline{CV}_T$):	0.067
Procedure:	Bubbler collection in 0.01 N sodium hydroxide, ion specific electrode	Validation Date:	8/1/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a midget bubbler containing 15 ml of 0.01 N sodium hydroxide to trap hydrogen bromide.
- 1.2 The resulting solution is diluted to 25 ml with 0.01 N sodium hydroxide and transferred to a 50-ml polyethylene beaker.
- 1.3 The diluted samples are analyzed using a bromide ion specific electrode.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 6.14-20.37 mg/cu m at an atmospheric temperature and pressure of 22°C and 763 mm Hg, using a 100-liter sample. The probable useful range of this method is 1-30 mg/cu m for 100-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for hydrogen bromide was determined to be 1.00 when sampled for 100 minutes at 1.0 liter per minute from a test atmosphere containing 20.37 mg/cu m.

3. Interference

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

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 6.14-20.37 mg/cu m was 0.067. This value corresponds to a standard deviation of 0.67 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 A collection efficiency of 1.00 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.9% 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 in paragraph 10.4.

5. Advantages and Disadvantages of the Method

- 5.1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is the use of bubblers to collect the analyte instead of a solid sorbent.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:
- 6.1.1 A glass "midget bubbler" containing the collection medium (Section 7.2).
- 6.1.2 A pump suitable for delivering at least 1.0 liter per minute for 100 minutes. 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.
- 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.

- 6.2 Volumetric flasks: 25-ml or convenient sizes.
- 6.3 Pipets: 1, 2, 4, and 5 ml.
- 6.4 Orion Model 94-35 bromide specific ion electrode, or equivalent.
- 6.5 Reference electrode, Orion 90-01 single junction, or equivalent calomel or silver/silver chloride electrode.
- 6.6 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.
- 6.7 Polyethylene beakers, 50-ml capacity.
- 6.8 Magnetic stirrer and stirring bars for 50-ml beakers.

7. Reagents

All chemicals must be ACS reagent grade or equivalent.

- 7.1 Doubly distilled water.
- 7.2 Collection Medium: 0.01 N sodium hydroxide solution. Dissolve 0.4 g of sodium hydroxide in 1 liter distilled water.
- 7.3 Sodium bromide, for preparation of standards.
- 7.4 Standard Bromide Solution.
 - 7.4.1 Dissolve 63.6 mg sodium bromide in 0.01 N sodium hydroxide (prepared from doubly distilled water) and dilute to 100 ml with 0.01 N sodium hydroxide. This solution is equivalent to 0.494 mg/ml Br^- . One ml of this solution contains the amount collected at 4.94 mg/cu m, when sampling at 1.0 liter per minute for 100 minutes. The 4.94 mg/cu m standard is made by spiking 15 ml of 0.01 N sodium hydroxide with 1 ml of the standard stock solution. Likewise, the 9.88 mg/cu m standard is prepared with 2 ml, and the 19.76 mg/cu m standard is prepared with 4 ml of the standard stock solution. The standards are diluted to 25 ml with 0.01 N sodium hydroxide prior to analysis with the bromide ion specific electrode.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with doubly distilled water.

8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pour 15 ml of the collection medium (Section 7.2) into the midget bubbler, using a graduated cylinder to measure the volume.

8.3.2 Connect the bubbler (via the adsorption tube) to the vacuum pump with a short piece of flexible tubing. The air being sampled should not pass through any other tubing or other equipment before entering the bubbler.

8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.0 liter per minute for 100 minutes. The flow rate should be known with an accuracy of $\pm 5\%$.

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

8.3.5 Terminate sampling at the predetermined time and note sample flow rate and collection time.

8.3.6 After sampling, the bubbler stem may be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1-2 ml of the collection medium, adding wash to the bubbler. Seal the bubbler with a Teflon or other non-reactive stopper prior to shipment.

8.3.7 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.3.8 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.

8.3.9 A "blank" bubbler should be handled in the same manner as the bubblers containing samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

8.4.1 The sample in each bubbler is analyzed separately.

8.4.2 Quantitatively transfer the contents of the bubbler bottle to a 25-ml volumetric flask. Make up to volume with 0.01 N sodium hydroxide.

8.4.3 Transfer the sample to a 50-ml polyethylene beaker and stir with a magnetic stirrer.

8.4.4 Lower the bromide ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mv) after it has stabilized (drift less than 0.5 mv/min).

9. Calibration and Standards

9.1 Prepare three bromide standard solutions as described in Section 7.4 at each of three levels (0.5X, 1X, and 2X the standard.

9.2 Insert the bromide ion specific electrode and the reference electrode into one of the standards at the 0.5X level, and stir the solution with the magnetic stirrer.

9.3 Record the resulting millivolt reading to the nearest 0.5 millivolt.

9.4 Repeat steps 9.2 and 9.3 for the remaining standard solutions.

9.5 Calibration standards at each level should be repeated twice daily.

9.6 Average the six millivolt readings at each level.

- 9.7 Prepare the standard curve by plotting the three averaged millivolt readings vs mg Br⁻ on semilog paper. Plot the mg Br⁻ on the log axis.

10. Calculations

- 10.1 Read the weight in mg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, because the standard curve is based on mg/25 ml volume, and the volume of the samples is identical to the volume of the standards.

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

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

where:

$$\text{mg sample} = \text{mg found in sample bubbler}$$

$$\text{mg blank} = \text{mg found in blank bubbler}$$

- 10.3 Calculate the mg of hydrogen bromide by multiplying the mg bromide ion found (Section 10.2) by 1.013, which is a conversion factor to convert mg Br⁻ to mg HBr.

- 10.4 The concentration of the analyte in air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000 \text{ liter/cu m}}{\text{Air volume sampled (liter)}}$$

- 10.5 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 analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

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

Hydrogen Fluoride

Analyte:	Hydrogen Fluoride	Method No.: S176
Matrix:	Air	Range: 1.33-4.50 mg/cu m
OSHA Standard:	3 ppm (2.45 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Bubbler collection in 0.1 N sodium hydroxide, ion specific electrode	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a midget bubbler containing 10 ml of 0.1 N sodium hydroxide to trap hydrogen fluoride.
- 1.2 The resulting solution is made up to 25 ml with 0.1 N sodium hydroxide and transferred to a 50-ml polyethylene beaker.
- 1.3 The sample is diluted with 25 ml total ionic strength activity buffer (TISAB).
- 1.4 The diluted samples are analyzed using a fluoride ion specific electrode.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 1.33-4.50 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg, using a 45-liter sample. The probable useful range of this method is 0.245-7.35 mg/cu m for 45-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for hydrogen fluoride was determined to be 0.991 ± 0.004 when sampled for 30 minutes at 1.5 liters per minute from a test atmosphere containing 4.50 mg/cu m.

3. Interference

- 3.1 When interferring 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 Hydroxide ion is the only significant electrode interference; however, addition of the TISAB eliminates this problem. Very large amounts of complexing metals such as aluminum may result in low readings even in the presence of TISAB.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.33-4.50 mg/cu m was 0.057. This value corresponds to a standard deviation of 0.14 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 A collection efficiency of 0.991 ± 0.004 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.5% higher 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 in paragraph 10.4.

5. Advantages and Disadvantages of the Method

- 5.1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.
- 5.2 There are no known disadvantages to the method.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:
 - 6.1.1 A glass "midget bubbler" containing the collection medium (Section 7.3). Bubbler stem unit consists of a two-hole rubber stopper to fit 1/8-in O.D. Teflon tubing.
 - 6.1.2 A prefilter unit which consists of the filter media and a polystyrene 37-mm, 2-piece cassette filter holder. The filter is a 37-mm mixed cellulose ester membrane filter with a 0.8-micrometer pore size. A cellulose backup pad should not be used, but care must be taken to insure that the filter is sealed tightly to avoid air leaks during sampling.

- 6.1.3 A pump suitable for delivering at least 1.5 liters per minute for 30 minutes. 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.
- 6.1.4 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.5 Thermometer.
- 6.1.6 Manometer.
- 6.1.7 Stopwatch.
- 6.2 Volumetric flasks: 25-ml or convenient sizes.
- 6.3 Pipets: 1, 2, 4, and 5 ml.
- 6.4 Orion Model 94-09 fluoride specific ion electrode, or equivalent.
- 6.5 Reference electrode, Orion 90-01 single junction, or equivalent calomel or silver/silver chloride electrode.
- 6.6 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.
- 6.7 Polyethylene beakers, 50-ml capacity.
- 6.8 Magnetic stirrer and stirring bars for 50-ml beakers.

7. Reagents

All chemicals must be ACS reagent grade or equivalent. Polyethylene beakers and bottles should be used for holding and storing all fluoride-containing solution.

- 7.1 Doubly distilled water.
- 7.2 Glacial acetic acid.
- 7.3 Collection Medium: 0.1 N sodium hydroxide solution. Dissolve 4 g of sodium hydroxide in 1 liter distilled water.
- 7.4 Sodium hydroxide, 5 N solution. Dissolve 20 g of sodium hydroxide in sufficient distilled water to give 100 ml of solution.
- 7.5 Sodium chloride.
- 7.6 Sodium citrate.

- 7.7 Total Ionic Strength Activity Buffer (TISAB). Place 500 ml of doubly distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in water bath (for cooling) and slowly add 5 N sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask and add doubly distilled water to the mark.
- 7.8 Sodium fluoride, for preparation of standards.
- 7.9 Standard Fluoride Solution.
- 7.9.1 Dissolve 12.06 mg sodium fluoride in 0.1 N sodium hydroxide (prepared from doubly distilled water) and dilute to 100 ml with 0.1 N sodium hydroxide. This solution is equivalent to 0.0546 mg/ml F^- . One ml of this solution contains the amount collected at the 0.5X OSHA level, when sampling at 1.5 liters per minute for 30 minutes. The 0.5X level standard is made by spiking 10 ml of 0.1 N sodium hydroxide with 1 ml of the standard stock solution. Likewise, the 1X level standard is prepared with 2 ml, and the 2X level is prepared with 4 ml of the standard stock solution. The standards are diluted to 25 ml with 0.1 N sodium hydroxide and 25 ml TISAB is added prior to analysis with the fluoride ion specific electrode.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with doubly distilled water.
- 8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Pour 10 ml of the collection medium (Section 7.3) into the midget bubbler, using a graduated cylinder to measure the volume.
- 8.3.2 Assemble the prefilter unit in the 2-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. A backup pad should not be used.
- 8.3.3 Connect the bubbler (via the adsorption tube) to the prefilter assembly and the vacuum pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and bubbler should be used. The air being sampled should not pass through any other tubing or other equipment before entering the bubbler.

- 8.3.4 Bubbler stem unit consists of a two-hole rubber stopper to fit 1/8-in O.D. Teflon tubing. One piece of tubing conducts the analyte vapor below the level of the collection medium where the analyte is trapped. The short outlet tube is connected to the sampling pump.
- 8.3.5 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.5 liters per minute for 30 minutes. The flow rate should be known with an accuracy of +5%.
- 8.3.6 The pump rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.
- 8.3.7 Terminate sampling at the predetermined time and note sample flow rate and collection time.
- 8.3.8 After sampling, the bubbler stem may be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1-2 ml of the collection medium, adding wash to the bubbler. Transfer the contents of the bubbler to a 50-ml polyethylene bottle. Rinse the bubbler with 2-3 ml of the collection medium and seal the bottle tightly for shipment.
- 8.3.9 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.
- 8.3.10 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.11 A "blank" bubbler should be handled in the same manner as the bubblers containing samples (fill, seal, and transport) except that no air is sampled through this bubbler.
- 8.3.12 The filter may be discarded since the method is designed to measure gaseous hydrogen fluoride only.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Quantitatively transfer the contents of the polyethylene bottle to a 25-ml volumetric flask. Make up to volume with 0.1 N sodium hydroxide.
- 8.4.3 Transfer the sample to a 50-ml polyethylene beaker. Add 25 ml of TISAB and stir with a magnetic stirrer.
- 8.4.4 Lower the fluoride ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mv) after it has stabilized (drift less than 0.5 mv/min).

9. Calibration and Standards

- 9.1 Prepare three fluoride standard solutions as described in Section 7.9 at each of three levels (0.5X, 1X, and 2X the standard).
- 9.2 Insert the fluoride ion specific electrode and the reference electrode into one of the standards at the 0.5X level, and stir the solution with the magnetic stirrer.
- 9.3 Record the resulting millivolt reading to the nearest 0.5 millivolt.
- 9.4 Repeat steps 9.2 and 9.3 for the remaining standard solutions.
- 9.5 Calibration standards at each level should be repeated twice daily.
- 9.6 Average the six millivolt readings at each level.
- 9.7 Prepare the standard curve by plotting the three averaged millivolt readings vs mg F^- on semilog paper. Plot the mg F^- on the log axis.

10. Calculations

- 10.1 Read the weight in mg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, because the standard curve is based on mg/50 ml volume, and the volume of the samples is identical to the volume of the standards.

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

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

where:

$$\text{mg sample} = \text{mg found in sample bubbler}$$

$$\text{mg blank} = \text{mg found in blank bubbler}$$

10.3 Calculate the mg of hydrogen fluoride by multiplying the mg fluoride ion found (Section 10.2) by 1.05, which is a conversion factor to convert mg F⁻ to mg HF.

10.4 The concentration of the analyte in air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000 \text{ liter/cu m}}{\text{Air volume sampled (liter)}}$$

10.5 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 analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 Elfers, L.A. and C.E. Decker, "Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode," Anal. Chem., 40 (11), p. 1658 (1968).

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

Phenol

Analyte:	Phenol	Method No.:	S330
Matrix:	Air	Range:	9.46-37.8 mg/cu m
OSHA Standard:	5 ppm (19 mg/cu m)-skin	Precision ($\overline{CV}_T$):	0.068
Procedure:	Bubbler collection in dilute sodium hydroxide: GC analysis of the collected samples after acidification with sulfuric acid	Validation Date:	8/1/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a midget bubbler containing 15 ml of 0.1 N sodium hydroxide to trap the phenol vapors present.
- 1.2 The resulting solution is acidified with sulfuric acid.
- 1.3 An aliquot of the collected sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with the areas for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 9.46-37.8 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the analytical method recovery is adequate.

3. Interference

- 3.1 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 proof of chemical identity.

- 3.2 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 9.46-37.8 mg/cu m was 0.068. This value corresponds to a 1.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 A collection efficiency of 1.00 ± 0.01 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.6% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in paragraph 10.3.

5. Advantages and Disadvantages of the Method

- 5.1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:
- 6.1.1 A standard glass midget bubbler containing the collection medium (Section 7.4).
- 6.1.2 A pump suitable for delivering at least 1 liter per minute for 100 minutes. The sampling pump is protected from splasher 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.
- 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.

- 6.2 Gas chromatograph equipped with a flame ionization detector.
- 6.3 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 35/60 mesh Tenax.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.
- 6.6 Volumetric flasks: convenient sizes for making solutions.
- 6.7 Pipets: 15 ml or other convenient sizes.

7. Reagents

- 7.1 Distilled water.
- 7.2 Phenol, reagent grade.
- 7.3 Sulfuric acid, reagent grade.
- 7.4 Collection medium, 0.1 N sodium hydroxide. Dissolve 4.0 g of sodium hydroxide in distilled water and dilute to a final volume of 1 liter.
- 7.5 Purified nitrogen.
- 7.6 Purified hydrogen.
- 7.7 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples.
 - 8.3.1 Pour 15 ml of the collection medium (Section 7.4) into each midget bubbler.
 - 8.3.2 Connect the midget bubbler with a 5-cm glass adsorption tube (6-mm I.D. and 8-mm O.D.) containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

- 8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, the time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute. A sample size of 100 liters is recommended.
- 8.3.4 After sampling, the bubbler stem may be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1 ml of distilled water, adding the wash to the bubbler. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
- 8.3.5 Care should be taken to minimize spillage or loss by evaporation.
- 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.7 A "blank" bubbler should be handled in the same manner as the bubblers containing samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Transfer the solution to a 25-ml volumetric flask.
- 8.4.3 Rinse the bubbler twice with 1 ml of distilled water and add the rinses to the flask.
- 8.4.4 Add 0.1 ml of concentrated sulfuric acid to the flask and mix. Check with pH paper to make sure that the pH is less than 4.
- 8.4.5 Dilute to mark with distilled water and mix.
- 8.4.6 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector

3. 500 ml/min (50 psig) air flow to detector
4. 215°C injector temperature
5. 225°C manifold temperature (detector)
6. 200°C column temperature

The glass inlet on the GC should be cleaned at the end of each day with water and acetone rinses. Reinsert the glass inlet into the injection port and let it bake out overnight.

- 8.4.7 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 distillation 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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.
- 8.4.8 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable means of area measurement, and preliminary results are read from a standard curve prepared as discussed below in paragraph 9.

8.5 Standard Solutions

8.5.1 Procedure for preparing standard solutions. Six standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of analyte into 15 ml of 0.1 N sodium hydroxide in a 25-ml volumetric flask. The amount introduced is equivalent to that present in a 1-liter air sample. The standards are acidified with 0.1 ml of concentrated sulfuric acid and made up to volume with distilled water. The solution should be checked with pH paper to make sure that its pH is less than 3. A parallel blank is prepared in the same manner, except that no analyte is added. The standards and blank are analyzed in exactly the same manner as the samples in Section 8.4.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/sample. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting mg/sample 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 known day-to-day variations and variations during the same day of the FID response.

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/sample and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

$$\text{mg sample} = \text{mg found in sample bubbler}$$

$$\text{mg blank} = \text{mg found in blank bubbler}$$

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 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 analyte

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

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

Phenylhydrazine

Analyte:	Phenylhydrazine	Method No.: S160
Matrix:	Air	Range: 10.37-44.8 mg/cu m
OSHA Standard:	5 ppm (22 mg/cu m)--skin	Precision ($\overline{CV}_T$): 0.060
Procedure:	Bubbler collection, complexation, colorimetric	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 Phenylhydrazine is collected in a standard midget bubbler containing 0.1 N hydrochloric acid.
- 1.2 The resulting solution is reacted with phosphomolybdic acid to form a bluish green colored complex.
- 1.3 The strong absorption maximum at 730 nm is used as a quantitative measure of phenylhydrazine.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 10.37-44.8 mg/cu m, at an atmospheric temperature and pressure of 22°C and 761 mm Hg. The probable range of the method is 5-45 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where the absorbance is greater than the limits of the standard curve, the samples can be diluted with hydrochloric acid prior to color development to extend the upper limit of the range.
- 2.2 A concentration of 5 mg/cu m of phenylhydrazine can be determined in a 100-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 1 cm cell. Greater sensitivity could be obtained by use of a longer path length cell.

3. Interferences

- 3.1 Any hydrazine derivative will potentially interfere with this method. Other reducing agents such as ferrous salts may also interfere.
- 3.2 Aldehydes and ketones in the air may interfere, because of the potential formation of phenylhydrazones in the acid medium in the bubbler.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 10.37-44.8 mg/cu m was 0.060. This value corresponds to a 1.32 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 Reference 11.2.
- 4.2 A collection efficiency of 1.00 ± 0.01 was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. 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 samples, collected in bubblers, are analyzed by means of a quick, instrumental method.
- 5.2 Phenylhydrazine is slowly air-oxidized and is difficult to maintain known purity. Therefore, all analytical work is done using phenylhydrazine hydrochloride.

6. Apparatus

- 6.1 Sampling Equipment. The sampling method for the bubbler collection method consists of the following components:
- 6.1.1 A glass, standard midget bubbler with a stem which has a fritted glass end and containing 0.1 N HCl (Section 7.2). The fritted end should have porosity approximately equal to that of Corning EC (170-220 μ maximum pore diameter).
- 6.1.2 A pump suitable for delivering at least 1 liter per minute for 100 minutes. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.

- 6.2 Spectrophotometer. This instrument should be capable of measuring the developed color at 730 nm.
- 6.3 Matched glass cells or cuvettes, 1-cm path length.
- 6.4 Assorted laboratory glassware -- pipets, volumetric flasks, and graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

- 7.1 Distilled water.
- 7.2 Collection Medium. 0.1 N HCl. Fill a 1000 ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated HCl, mix and bring volume to the 1000 ml mark.
- 7.3 Phosphomolybdic acid solution (PMA). Dissolve 15 grams PMA in 500 ml distilled water, allow to stand one day and filter before use through a fluted paper filter.
- 7.4 Phenylhydrazine hydrochloride.
- 7.5 Phenylhydrazine hydrochloride, standard solution. Weigh accurately 0.1000 g phenylhydrazine hydrochloride in a 100-ml volumetric flask and fill to the mark with 0.1 N HCl.

8. Procedure

- 8.1 Cleaning of equipment. No specialized cleaning of glassware is required.
- 8.2 Calibration of personal pump. Personal sampling pump should be calibrated using integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Pour 15 ml of the 0.1 N HCl (Section 7.2) into each bubbler.
 - 8.3.2 Connect a bubbler with a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.
 - 8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute. A sample size of 100 liters is recommended.

- 8.3.4 After sampling the bubbler stems are lifted out of the bubbler bottom and rinsed with approximately 5 ml distilled water. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
- 8.3.5 Care should be taken to minimize spillage or loss by evaporation at all times.
- 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.7 A "blank" bubbler should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Transfer the solution to a 50-ml volumetric flask.
- 8.4.3 Rinse bubbler twice with 5 ml distilled water each and add rinses to volumetric flask.
- 8.4.4 Add 10 ml phosphomolybdic acid solution to volumetric flask. This may be carefully measured in a 10-ml graduated cylinder.
- 8.4.5 Dilute to the 50-ml mark with distilled water.
- 8.4.6 Pipet a 3-ml aliquot into a 10-ml volumetric flask and dilute to 10 ml with distilled water.
- 8.4.7 Read at 730 nm in the spectrophotometer against a blank prepared from the 0.1 N HCl in the same fashion as the samples.

9. Calibration and Standards

9.1 Preparation of the Calibration Curve.

- 9.1.1 To six 50-ml volumetric flasks, add 15 ml 0.1 N HCl using a 25-ml graduated cylinder.
- 9.1.2 Carefully pipet 1, 2, 3, 6, and 9 ml of the standard solution into the flasks (Section 7.5). Process one flask as a blank.

- 9.1.3 Add to this mixture 10 ml of phosphomolybdic acid solution (Section 7.3) using a 10-ml graduated cylinder.
- 9.1.4 Continue as described in Section 8.4.5.
- 9.1.5 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.
- 9.1.6 Read the blank in the sample cell, then read the samples at 730 nm.
- 9.1.7 Construct a calibration curve by plotting absorbance against equivalent milligrams of phenylhydrazine in the color developed solution. Since the calibration curve is made using aliquots of phenylhydrazine hydrochloride, the equivalent weight of phenylhydrazine must be calculated.

$$\begin{array}{lcl} \text{equivalent mg} & \text{mg phenyl-} & \\ \text{of phenyl-} & = \text{hydrazine} \cdot \text{HCl} & \times \frac{108.14}{144.6} \times \frac{\text{ml standard}}{100 \text{ ml}} \\ \text{hydrazine} & \text{weighed out} & \\ & \text{in standard} & \end{array}$$

where:

108.14 = molecular weight of phenylhydrazine

144.6 = molecular weight of phenylhydrazine·HCl

10. Calculations

- 10.1 Subtract the absorbance of the blank from the absorbance of each sample.
- 10.2 Determine from the calibration curve (Section 9.1.7) the mg of phenylhydrazine present in each sample.
- 10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg phenylhydrazine (Section 10.2)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 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 analyte

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 Leo Feinsilver, Joseph Perregrino, and Courtney Smith, Jr.,
"Estimation of Hydrazine and Three of Its Methyl Derivatives,"
Industrial Hygiene Journal, 20, February 1959, 26-31.
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No.
CDC-99-74-45.

Pyridine

Analyte:	Pyridine	Method No.: S161
Matrix:	Air	Range: 7.59-30.4 mg/cu m
OSHA Standard:	5 ppm (15 mg/cu m)	Precision ($\overline{CV}_T$): 0.059
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with methylene chloride.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 7.59-30.4 mg/cu m at an atmospheric temperature and pressure of 22°C and 763 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 1.5-45 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4.5-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of pyridine and other substances in the air. The first section of the charcoal tube was found to hold at least 6.8 mg of pyridine when a test atmosphere containing

30.4 mg/cu m of pyridine in air was sampled at 0.93 liter per minute for 240 minutes; at that time the concentration of pyridine in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 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. Since methylene chloride is used rather than carbon disulfide to desorb pyridine from the charcoal, it would not be possible to measure methylene chloride in the sample with this desorbing solvent. If it is suspected that methylene chloride is present, a separate sample should be collected for methylene chloride analysis.
- 3.3 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 proof of chemical identity.
- 3.4 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 7.59-30.4 mg/cu m was 0.059. This value corresponds to a 0.9 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 Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.3% higher 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 in paragraph 10.5.

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 tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 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 the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, 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 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.2).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 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 one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% Carbowax 20M on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

- 6.8 Pipets: 1.0-ml delivery pipets.
- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.
- 7. Reagents
 - 7.1 Chromatographic quality methylene chloride.
 - 7.2 Pyridine, reagent grade.
 - 7.3 Purified nitrogen.
 - 7.4 Prepurified hydrogen.
 - 7.5 Filtered compressed air.
- 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 charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 A maximum sample size 100 liters is recommended. Sample at a flow of 1.0 liter per minute or less. 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 charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of methylene chloride 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.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 3. 500 ml/min (50 psig) air flow to detector
 4. 260°C injector temperature
 5. 285°C manifold temperature (detector)
 6. 140°C column temperature
- 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 distillation

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.

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

8.5 Determination of Desorption Efficiency

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of pyridine containing 393 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 100-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. 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 compound into 1.0 ml of methylene chloride 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 analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 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 known day-to-day variations and variations during the same day of the FID response.

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 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.

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

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 get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 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 analyte
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 No. CDC-99-74-45.

Sulfuric Acid

Analyte:	Sulfuric Acid	Method No.: S174
Matrix:	Air	Range: 0.561-2.577 mg/cu m
OSHA Standard:	1 mg/cu m	Precision ($\overline{CV}_T$): 0.082
Procedure:	Filter collection, titration with barium perchlorate	Validation Date: 8/1/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a cellulose membrane filter to collect particulate matter.
- 1.2 The filter is transferred to a screw cap bottle and extracted with distilled water and isopropyl alcohol.
- 1.3 The pH of the sample is adjusted with dilute perchloric acid.
- 1.4 The resulting solution is titrated with 0.005 M barium perchlorate using Thorin as the indicator. There is a sharp change from yellow to apricot at the end point.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.561-2.577 mg/cu m at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 180-liter sample. The probable useful range of this method is 0.1-3 mg/cu m for 180-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for sulfuric acid was determined to be 0.967 ± 0.030 when sampled for 120 minutes at 1.5 liters per minute from a test atmosphere containing 2.577 mg/cu m.

3. Interference

- 3.1 When any sulfate containing compounds other than sulfuric acid are known or suspected to be present in the air, such information,

including their suspected identities, should be transmitted with the sample.

3.2 Metal ion interferences can be eliminated by passing the solution through a cation exchange resin.

3.3 Concentrations of phosphate ions greater than the sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.561-2.577 mg/cu m was 0.082. This value corresponds to a standard deviation of 0.082 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.6.

4.2 A collection efficiency of 0.967 ± 0.030 (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency was necessary, and it is assumed that no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. 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. Samples collected on filters are analyzed by means of a rapid titration method.

5.2 This method does not distinguish between sulfuric acid and other sulfates collected on the filter. Since this method measures total sulfate, the acidity of the samples should be measured to determine the fraction of the sulfate that is in the acid form.

6. Apparatus

6.1 The unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 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 $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

- 6.1.3 Thermometer.
- 6.1.4 Manometer.
- 6.1.5 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 supported by a cellulose backup pad.
- 6.3 Screw cap bottles. Within 1 hour after the sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping.
- 6.4 Erlenmeyer flasks, 125 ml.
- 6.5 Pipets, 2 ml or convenient sizes.
- 6.6 Burette. A burette of 10-ml capacity graduated in 0.05 ml.
- 6.7 Daylight fluorescent lamp aids in identifying the end point.
- 6.8 Ion Exchange Resin. Dowex 50W-X8, 20/50 mesh, hydrogen form ion exchange columns may be constructed using glass burettes or tubing. A column with an inside diameter of 8 mm and 7 inches of resin has a capacity of approximately 25 milliequivalents. This is used to purify the standard sulfate solution and for samples which might contain possible interfering metal ions. When about two-thirds of the resin's capacity has been exhausted (deterioration in sharpness of the endpoint), regenerate the resin by passing 30 ml of 4 M hydrochloric acid through the column.

After charging and thorough washing with distilled water, the column is ready for use.

- 6.9 Volumetric flasks, 1 liter, or convenient sizes for preparation of standard solutions.

7. Reagents

- 7.1 Doubly distilled water.
- 7.2 Isopropanol, reagent grade.
- 7.3 Anhydrous sodium sulfate, reagent grade. Prepare a 0.005 M sodium sulfate solution by dissolving 0.7393 g anhydrous sodium sulfate in approximately 100 ml distilled water. Pass this solution slowly through the ion exchange resin and collect the solution in a clean 1-liter volumetric flask. Rinse the column with additional amounts of distilled water (approximately 300 ml), also collecting the rinse in the flask. Make up to volume with distilled water and mix thoroughly.

- 7.4 Barium Perchlorate, 0.005 M. Dissolve 2.0 g of barium perchlorate trihydrate in a 1-liter volumetric flask with distilled water and make up to volume. Standardize the solution against the sodium sulfate standard. Into a 125-ml erlenmeyer flask, pipet 5 ml of the sodium sulfate standard and 40 ml of isopropanol. Adjust the pH to 3.5 with perchloric acid. Add 3 drops of Thorin, and titrate against barium perchlorate to the end point.
- 7.5 Hydrochloric Acid, 4 M. Add 300 ml concentrated hydrochloric acid to 600 ml distilled water. The hydrochloric acid is used to regenerate the ion exchange column.
- 7.6 Perchloric Acid, 1.8%. Dilute 25 ml of reagent grade perchloric acid (70-72%) to 1 liter with distilled water.
- 7.7 Thorin. Prepare a 0.1%-0.2% solution in distilled water.
- 7.8 Concentrated nitric acid.
- 7.9 Concentrated sulfuric acid.
- 7.10 pH paper, Hydrion.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis, as well as the screw cap bottles, should be detergent washed and thoroughly rinsed with tap water and distilled water, followed by acid washing in concentrated nitric acid. Rinse with distilled water.
 - 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.
 - 8.3.2 Remove the cassette plugs and attach 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 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm 5\%$.
 - 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 pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.
 - 8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
 - 8.3.7 The cellulose filter should be removed from the cassette filter holder and the cellulose backup pad with 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.
 - 8.3.8 Carefully record the sample identity and all relevant sampling data.
 - 8.3.9 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.
 - 8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.
- 8.4 Analysis of Samples
- 8.4.1 Open the screw cap bottle containing the filter, and pipet 2 ml of distilled water into the bottle. Let it stand for 5-10 minutes.
 - 8.4.2 Transfer the rinse to a 125-ml erlenmeyer flask.
 - 8.4.3 Add 3 ml isopropyl alcohol to the screw cap bottle, and let it stand for 5-10 minutes.
 - 8.4.4 Transfer the isopropyl alcohol-rinse to the erlenmeyer flask. Repeat steps 8.4.3 and 8.4.4 once more.
 - 8.4.5 Add an additional 10 ml isopropyl alcohol to the erlenmeyer flask.

- 8.4.6 Adjust the pH of the solution in the flask with 1.8% perchloric acid to a value between 2.5-4.0. One or two large drops of the perchloric acid should be enough to adjust the pH.
- 8.4.7 Add 3 drops of Thorin to the erlenmeyer flask.
- 8.4.8 Titrate the sample with 0.005 M barium perchlorate to an apricot-colored end point.

8.5 Determination of Analytical Method Recovery

- 8.5.1 Need for determination. It is anticipated that the extraction scheme is dependent on operator skill and perhaps on the formulation used to disperse the analyte. Thus, it is necessary to determine the recovery of the analyte.
- 8.5.2 Procedure for determining analytical method recovery. Dilute 1 ml of concentrated sulfuric acid in a 50-ml volumetric flask with distilled water. Titrate a 100-microliter aliquot of this solution against the standardized barium perchlorate solution to determine the molarity of the sulfuric acid. For titration, place a 100-microliter aliquot of the sulfuric acid solution into a 125-ml erlenmeyer flask and add 5 ml distilled water, 40 ml isopropanol, and adjust the pH to 4.0 by adding 1.8% perchloric acid dropwise. Add three drops of Thorin and titrate to an end point. The molarity of the standardized sulfuric acid should be approximately 0.37 M. A known amount of the standardized sulfuric acid solution, 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 and analyzed as described in Section 8.4. An amount of the analyte equivalent to that present in a 180-liter sample at the selected level is used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are then extracted and analyzed as described 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

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

9. Calibration and Standards

The barium perchlorate solution is standardized by titrating the ion exchanged sodium sulfate standard to the end point with Thorin as the indicator. (See Section 7.4) The molarity of $\text{Ba}(\text{ClO}_4)_2$ is calculated as follows:

$$M_{\text{Ba}(\text{ClO}_4)_2} = \frac{\text{ml}_{\text{Na}_2\text{SO}_4} \times M_{\text{Na}_2\text{SO}_4}}{\text{ml}_{\text{Ba}(\text{ClO}_4)_2}}$$

where:

$$\text{ml}_{\text{Na}_2\text{SO}_4} = \text{ml Na}_2\text{SO}_4 \text{ solution needed to titrate Ba}(\text{ClO}_4)_2$$

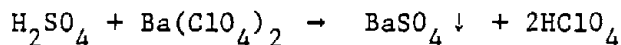
$$M_{\text{Na}_2\text{SO}_4} = \text{Molarity of Na}_2\text{SO}_4$$

$$\text{ml}_{\text{Ba}(\text{ClO}_4)_2} = \text{ml Ba}(\text{ClO}_4)_2 \text{ used}$$

The molarity of $\text{Ba}(\text{ClO}_4)_2$ should be checked periodically.

10. Calculations

10.1 The following reaction is the basis for this analytical method.



10.2 The mg of H_2SO_4 can be calculated as follows:

$$\text{mg H}_2\text{SO}_4 = M_{\text{Ba}(\text{ClO}_4)_2} \times \text{ml}_{\text{Ba}(\text{ClO}_4)_2} \times 98$$

where:

$$M_{\text{Ba}(\text{ClO}_4)_2} = \text{Molarity of Ba}(\text{ClO}_4)_2 \text{ solution.}$$

$$\text{ml}_{\text{Ba}(\text{ClO}_4)_2} = \text{ml of Ba}(\text{ClO}_4)_2 \text{ solution needed to titrate the sample.}$$

$$98 = \text{Molecular weight of H}_2\text{SO}_4.$$

10.3 Corrections for the blank must be made for each sample if an end point can be seen from the blank filter.

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

where:

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

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

10.4 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.5 The concentration of H_2SO_4 can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ liter/cu m}}{\text{Air Volume Sampled (liter)}}$$

11. References

- 11.1 Fritz, J.S., and Yamamura, S.S., Anal. Chem., 27, 1461 (1955).
- 11.2 Leithe, W., "The Analysis of Air Pollutants," Ann Arbor Science Press, 1970.
- 11.3 Kundig, Chem. Rundschau, 18, 123 (1965).
- 11.4 Fielder and Morgan, Anal. Chem. Acta, 23, 538 (1960).
- 11.5 Fielder and Morgan, Z. Anal. Chem., 183, 455 (1961).
- 11.6 Documentation of NIOSH Validation, NIOSH Contract No. CDC-99-74-45.

o-Toluidine

Analyte:	o-Toluidine	Method No.: S168
Matrix:	Air	Range: 11.72-46.9 mg/cu m
OSHA Standard:	5 ppm (22 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.060
Procedure:	Adsorption on silica gel, desorption with 95% ethanol, GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.
- 1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 95% ethanol.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 11.72-46.9 mg/cu m at an atmospheric temperature and pressure of 22°C and 759 mm Hg, using a 55-liter sample. Under the conditions of sample size (55 liters) the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3-mg sample. The 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 silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 10.4 mg of analyte when a test atmosphere containing

46.9 mg/cu m of analyte in air was sampled at 0.922 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

- 3.1 Silica gel has a high affinity for water, so organic vapors may not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.
- 3.2 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.
- 3.3 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 proof of chemical identity.
- 3.4 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 11.72-46.9 mg/cu m was 0.060. This value corresponds to a 1.32 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 Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.6% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in paragraph 10.5.

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 tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 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 the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, 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 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate.
- 6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 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 one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (2-ft x 1/8-in stainless steel) packed with Chromosorb 103 (80/100 mesh).
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Ultrasonic bath.

6.8 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.9 Pipets: 1.0-ml delivery pipets.

6.10 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Ethanol, 95%.

7.2 o-Toluidine, reagent grade.

7.3 n-Hexane, reagent grade.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

7.6 Purified nitrogen.

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 silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

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

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

8.3.5 A sample size of 50 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rate should be known with an accuracy of at least +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 silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 95% ethanol is pipetted into each sample container. The sample is desorbed for one hour using an ultrasonic bath to aid desorption. Note that the water in the ultrasonic bath can get hot (ca. 50-60°C) during the desorption period. Therefore, all vials must be tightly capped to minimize evaporation losses.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 240°C injector temperature
 - 5. 265°C manifold temperature (detector)
 - 6. 180°C column temperature

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 distillation 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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm. A known amount of hexane solution of o-toluidine containing 0.275 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 50-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X OSHA standard levels) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. 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 compound into 1.0 ml of 95% ethanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) is dependent on the amount of analyte collected on the silica gel. The desorption efficiency 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 analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml 95% ethanol, because samples are desorbed in this amount of 95% ethanol. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, are 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 the 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.

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 95% ethanol and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 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 analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

References

- 11.1 E.E. Campbell, G.O. Wood, and R.G. Anderson, Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR, and LA-5634-PR, Los Alamos, N.M., Nov. 1972, Jan. 1973, June 1973, Aug. 1973, Dec. 1973, and June 1974.
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Xylidine
(2,4-Dimethylaminobenzene)

Analyte:	Xylidine	Method No.: S162
Matrix:	Air	Range: 12.5-50.0 mg/cu m
OSHA Standard:	5 ppm (25 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on silica gel, Validation Date: 8/1/75 desorption with 95% ethanol, GC	

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.
- 1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 95% ethanol.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 12.5-50.0 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 2.5-75 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1.5-mg sample. The 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 silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 2.22 mg of analyte when a test atmosphere containing

50.0 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

- 3.1 Silica gel has a high affinity for water, so organic vapors may not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.
- 3.2 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.
- 3.3 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 proof of chemical identity.
- 3.4 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 12.5-50.0 mg/cu m was 0.057. This value corresponds to a 1.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.4% higher 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 in paragraph 10.5.

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 tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 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 the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, 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 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. Reference 11.3
- 6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 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 one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (2-ft x 1/8-in stainless steel) packed with Chromosorb 103 (80/100 mesh).
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Ultrasonic bath.

6.8 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.9 Pipets: 1.0-ml delivery pipets.

6.10 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Ethanol, 95%.

7.2 Xylidine (2,4-Dimethylaminobenzene), reagent grade.

7.3 n-Hexane, reagent grade.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

7.6 Purified nitrogen.

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 silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

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

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

8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±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 silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 95% ethanol is pipetted into each sample container. The sample is desorbed for one hour using an ultrasonic bath to aid desorption. Note that the water in the ultrasonic bath can get hot (ca. 50-60°C) during the desorption period. Therefore, all vials must be tightly capped to minimize evaporation losses.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 230°C injector temperature
 - 5. 235°C manifold temperature (detector)
 - 6. 170°C column temperature

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 distillation 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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm. A known amount of hexane solution of xylydine containing 125 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X OSHA standard levels) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. 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 compound into 1.0 ml of 95% ethanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) is dependent on the amount of analyte collected on the silica gel. The desorption efficiency 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 analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml 95% ethanol, because samples are desorbed in this amount of 95% ethanol. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, are 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 the 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.

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 95% ethanol and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 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 analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

References

- 11.1 E.E. Campbell, G.O. Wood, and R.G. Anderson, Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR, and LA-5634-PR, Los Alamos, N.M., Nov. 1972, Jan. 1973, June 1973, Aug. 1973, Dec. 1973, and June 1974.
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

