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SECOND EDITION

Part II
Standards Completion Program Validated Methods

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Manual Coordinator

VOLUME 3

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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Mr. John V. Crable and Dr. David G. Taylor, respectively Chief and Assistant Chief of the Measurements Research Branch, were responsible for the development and preparation of this Manual.

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Analyte:	o-Dichlorobenzene	Method No.:	S135
Matrix:	Air	Range:	150-629 mg/cu m
OSHA Standard:	50 ppm (300 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.067
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 150-629 mg/cu m at an atmospheric temperature and pressure of 28°C and 760 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 29.9 mg of analyte when a test atmosphere containing 655 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; i.e. at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. The breakthrough data are based on a prior experiment.

(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 as 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 150-629 mg/cu m was 0.067. This value corresponds to a 20 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 2.4% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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% OV-101 on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 o-Dichlorobenzene, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 of 3 liters is recommended. This can be accomplished by sampling for 15 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.

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

8.3.7 The 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

11.1 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.

Diazomethane

Analyte:	Diazomethane	Method No.:	S137
Matrix:	Air	Range:	0.17-0.80 mg/cu m
OSHA Standard:	0.2 ppm (0.4 mg/cu m)	Precision ($\overline{CV}_T$):	0.084
Procedure:	Adsorption on coated resin, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

1.1 A known volume of air is drawn through a tube containing XAD-2 resin coated with octanoic acid to trap the diazomethane present.

1.2 The coated XAD-2 resin 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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.17-0.80 mg/cu m at an atmospheric temperature and pressure of 26.0°C and 765 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 0.10-1.2 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12 µg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the coated XAD-2 resin tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the coated XAD-2 resin tube was found to hold at least 45 µg of analyte when a test atmosphere containing 0.83 mg/cu m of analyte in air was sampled at 0.22 liters per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. The collection efficiency and reaction of diazomethane with the octanoic acid-coated resin may be strongly dependent on sample flow rates, therefore all samples must be collected at a flow rate of 0.2 liters per minute only.

(The resin tube consists of two sections of coated XAD-2 resin separated by a section of silylated glass wool. 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 The adsorptive capacity of XAD-2 resin is not severely affected by water vapor. Breakthrough volume will not be substantially affected by high relative humidity.

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 as 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 0.17-0.80 mg/cu m was 0.084. This value corresponds to a 0.03 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 On the average, the concentrations obtained at 1X and 2X the OSHA standard level using the overall sampling and analytical method were 10% lower than the "true" concentrations for a limited number of laboratory experiments. At 0.5X the OSHA standard level, the concentration found was 30% lower than the "true" concentration. The difference between the "found" and "true" concentrations may represent a bias in the sampling method due to incomplete conversion of diazomethane and octanoic acid into methyl octanoate. Therefore, a recovery correction should be applied to the final result; for the specific recovery correction factor, refer to the Diazomethane S137 Backup Data Report.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can

be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the resin 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 ±5% at the recommended flow rate. (Reference 11.2)

6.2 Resin tubes: glass tube with both ends flame-sealed, 7 cm long with 6 mm O.D. and 4 mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin, coated with 1% octanoic acid, prepared as described in Section 7.7. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the outlet end of the tube and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. 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% SP-1000 stationary phase on 100/120 mesh Supelcoport, preceded by a short (6" x 1/8" stainless steel) precolumn packed with 10% Carbowax 20 M and 1.2% NaOH on 80/100 mesh Gas Chrom Q. (This column combination eliminates interference from excess octanoic acid. Replace this pre-column when evidence of background contamination and erratic chromatograms begin to show-up.)

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, graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methyl octanoate, reagent grade

7.3 Tridecane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 Filtered compressed air

7.7 Octanoic acid-coated resin: the XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. It must be washed before use by packing into a column (length to diameter ratio ~ 10:1) and washing with 3 bed volumes of methanol and 2 bed volumes of pentane. The effluent washings should be checked by GC at the sensitivity required for later analyses to be sure there are no interfering peaks. The clean resin should be dried at room temperature.

In order to prepare the coated resin, weigh out ~ 10 g of washed and dried XAD-2 into a round-bottomed flask. Add ~ 25 ml of a volatile solvent such as acetone (not methanol). To the sorbent/solvent slurry add, via microliter syringe, a quantity of reagent grade octanoic acid equivalent to 1% of the sorbent weight. Attach the flask to a rotary evaporator and allow the sorbent to tumble under vacuum until the solvent has evaporated. The coated resin should then be allowed to dry at room temperature.

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 XAD-2 resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, 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 coated XAD-2 resin is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The coated XAD-2 resin tube should be placed in a vertical direction during sampling to minimize channeling through the resin.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the coated XAD-2 resin tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute only. 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 coated XAD-2 resin 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 coated XAD-2 resin tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each coated XAD-2 resin tube is scored with a file in front of the first section of coated XAD-2 resin and broken open. The glass wool is removed and discarded. The XAD-2 resin in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of glass wool is removed and discarded and 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is

added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 95°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 technique.

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 may vary from one laboratory to another and also from one batch of coated XAD-2 resin 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 coated XAD-2 resin is used.

8.5.2 Procedure for determining desorption efficiency. Coated resin 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 resin must be from the same batch as that used in obtaining the samples and can be obtained from unused coated XAD-2 resin tubes. The open end is capped with Parafilm. A known amount of methyl octanoate is injected directly into the coated resin 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.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the coated XAD-2 resin. 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

The desorption efficiency is dependent on the amount of analyte collected on the resin. 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 µg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the methyl octanoate is used to convert µg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in µg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in µg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 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.

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

where:

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

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2 for the amount found in the front section). Divide the total weight by this desorption efficiency to obtain the corrected µg/sample as methyl octanoate. To convert µg of methyl octanoate to µg of diazomethane, multiply the corrected µg/sample by the molecular weight ratio: 42.01/158.2

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight of methyl octanoate}}{\text{D.E.}} \times \frac{42.01}{158.2}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{\text{Air Volume Sampled (liters)} \times \text{Recovery Factor}}$$

where:

Recovery Factor is 0.70 for 0.5X, 0.90 for 1X and 2X.

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

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

where:

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

11. References

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

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

Diethylamine

Analyte:	Diethylamine	Method No.:	S139
Matrix:	Air	Range:	37.6 - 165 mg/cu m
OSHA Standard:	25 ppm (75 mg/cu m)	Precision ($\overline{CV}_T$):	0.070
Procedure:	Adsorption on silica gel, desorption with 0.2 N H_2SO_4 in 10% methanol, GC	Validation Date:	6/6/75

1. Principle of the Method

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 0.2 N H_2SO_4 in 10% methanol.

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 37.6 - 165 mg/cu m at an atmospheric temperature and pressure of 29.5°C and 757 mm Hg, using a 50-liter sample. Under the conditions of sample size (50 liters), the probable useful range of this method is 15-225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 11-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 7.3 mg of analyte when a test atmsophere containing

160.5 mg/cu m of analyte in air was sampled at 0.19 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 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 a methanolic solution is used to desorb the analyte from the silica gel, it is not possible to measure methanol in the sample with this desorbing solvent. If it is suspected that methanol is present, a separate sample should be collected for methanol 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 37.6 - 165.1 mg/cu m was 0.070. This value corresponds to a 5.25 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.4% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

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 30 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 (6-ft x 1/4-in glass, 2 mm ID) packed with 4% Carbowax 20M + 0.8% KOH on Carbosieve B.

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

6.6 Two-milliliter sample containers with Teflon-lined caps.

6.7 Ultrasonic bath.

6.8 Microliter syringes: 10-microliter, 500-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 0.2 N H_2SO_4 in 10% methanol (10 parts methanol + 90 parts water).

7.2 0.3 N potassium hydroxide.

7.3 Diethylamine, reagent grade.

7.4 n-Propanol, or other suitable internal standard.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

7.7 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 glass vial with Teflon-lined cap. The separating section of foam is removed and discarded: the second section is transferred to another capped vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 0.2 N H_2SO_4 in 10% methanol is pipetted into each sample container. The sample is desorbed for 3 hours using an ultrasonic bath to aid desorption. Tests indicate that a 3-hour desorption period is necessary for adequate desorption of the analyte. 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 Neutralization of Samples.

1. Allow the silica gel particles to settle for a few minutes.

2. Withdraw a 500-microliter aliquot of the clear supernatant liquid and transfer to a 1.0 ml stoppered or Teflon-capped container. A 500-microliter syringe is recommended to minimize disturbing the silica gel bed and the potential transfer of silica particles. Note that the neutralization reaction should never be done in the presence of silica gel, because low recovery will be obtained; this is probably due to readsorption and/or decomposition.

3. Add 500 microliters of the 0.3 N potassium hydroxide solution.

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

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

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (50 psig) air flow to detector
4. 155°C injector temperature
5. 200°C manifold temperature (detector)
6. 70°C column temperature

8.4.5 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. One microliter of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 1-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since all the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample

occupies 1.0 microliter 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.

8.4.6 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as 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. 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 the analyte 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 0.5X, 1X and 2X OSHA standard level. Six tubes 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 2.0 ml of a 1:1 mixture of the 0.2 N H_2SO_4 and 0.3 N KOH solutions 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 per 2.0 ml acid-base mixture, because samples are desorbed and diluted in this equivalent amount of acid-base mixture. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 2.0 ml versus peak area.

For the internal standard method, use the acid-base mixture (1+1) containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per 2 ml is plotted versus the area ratio of the analyte to that of the internal standard.

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/2.0 ml solvent, and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front 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.

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

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

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

where:

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

11. Reference

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

Dimethylamine

Analyte:	Dimethylamine	Method No.:	S142
Matrix:	Air	Range:	7.02 - 29.5 mg/cu m
OSHA Standard:	10 ppm (18 mg/cu m)	Precision ($\overline{CV}_T$):	0.062
Procedure:	Adsorption on silica gel, desorption with 0.2 N H_2SO_4 in 10% methanol, GC	Validation Date:	6/6/75

1. Principle of the Method

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 0.2 N H_2SO_4 in 10% methanol.

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 7.02 - 29.5 mg/cu m at an atmospheric temperature and pressure of 28.5°C and 758 mm Hg, using a 48-liter sample. Under the conditions of sample size (50 liters) the probable useful range of this method is 3.6 - 54 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.7 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 1.94 mg of analyte when a test atmosphere containing 42.5 mg/cu m of analyte in air was sampled at 0.19 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 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 a methanolic solution is used to desorb the analyte from the silica gel, it is not possible to measure methanol in the sample with this desorbing solvent. If it is suspected that methanol is present, a separate sample should be collected for methanol 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 7.02 - 29.5 mg/cu m was 0.062. This value corresponds to a 1.1 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.1% 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.

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 ± 5% at the recommended flow rate.

6.2 Silica gel tubes: Separate front and backup glass tubes with both ends of each tube flame-sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D. Each tube contains the appropriate amount of 20/40 mesh silica gel. The front adsorbing tube contains approximately 150 mg of silica gel, the backup tube, approximately 75 mg. A plug of silylated glass wool is placed at each end of the silica gel tubes. 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. Column (6-ft x 1/4-in glass. 2 mm ID) packed with 4% Carbowax 20M + 0.8% KOH on Carbosieve B.

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

6.5 Two-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.6 Microliter syringes: 10-microliter, 500-microliter, and other convenient sizes for making standards.

6.7 Pipets: 1.0-ml delivery pipets.

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

7. Reagents

7.1 0.2 N sulfuric acid in 10% methanol (10 parts methanol + 90 parts water)

7.2 0.3 N potassium hydroxide

7.3 Dimethylamine, 99%

7.4 Dimethylamine hydrochloride, reagent grade

7.5 Isopropyl alcohol, or other suitable internal standards

7.6 Prepurified hydrogen

7.7 Filtered compressed air

7.8 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 tubes 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 $\pm$ 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 is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml glass vial with Teflon-lined cap. The separating section of foam is removed and discarded; the second section is transferred to another capped vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 0.2 N H_2SO_4 in 10% methanol is pipetted into each sample container. The sample is desorbed for 3 hours using an ultrasonic bath to aid desorption. Tests indicate that a 3-hour desorption period is necessary for adequate desorption of the analyte. 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 Neutralization of Samples

1. Allow the silica gel particles to settle for a few minutes.

2. Withdraw a 500-microliter aliquot of the clear supernatant liquid and transfer to a 1.0 ml stoppered or Teflon-capped container. A 500-microliter syringe is recommended to minimize disturbing the silica gel bed and the potential transfer of silica particles. Note that the neutralization reaction should never be done in the presence of silica gel, because low recovery will be obtained; this is probably due to readsorption and/or decomposition.

3. Add 500 microliters of the 0.3 N potassium hydroxide solution.

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

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

1. 30 ml/min (24 psig) nitrogen carrier gas flow

2. 30 ml/min (25 psig) hydrogen gas flow to detector

3. 300 ml/min (50 psig) air flow to detector

4. 155°C injector temperature

5. 200°C manifold temperature (detector)

6. 60°C column temperature

8.4.5 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. One microliter of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 1-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since all the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample

occupies 1.0 microliter 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. 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 tubes containing only the first section of the sampling tube (approximately 150 mg) are used. These silica gel tubes must be from the same batch as those used for the samples. A known amount of the dimethylamine gas is injected directly into the activated silica gel tubes with a gas-tight syringe of appropriate capacity, and the tube is tightly capped at both ends with plastic caps.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 50-liter sample at the selected level. The tubes are 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 as described in Section 9.

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 per 2.0 ml of acid-base mixture, because samples are desorbed and diluted in this equivalent amount of solvent. The dimethylamine hydrochloride may be used to prepare standard solutions by weighing known amounts of dimethylamine hydrochloride which would correspond to the desired amount of dimethylamine and dissolving the compound in a 1:1 mixture of the 0.2N sulfuric acid in 10% methanol and the 0.3N potassium hydroxide solution. 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 per 2.0 ml versus peak area.

For the internal standard method, use the acid-base mixture (1:1) containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard.

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/2.0 ml solvent, and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front 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.

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

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

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

where:

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

11. Reference

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

1,1-Dimethylhydrazine

Analyte:	1,1-Dimethylhydrazine	Method No.: S143
Matrix:	Air	Range: 0.506-2.22 mg/cu m
OSHA Standard:	0.5 ppm (1 mg/cu m) - skin	Precision (CV_T): 0.062
Procedure:	Bubbler collection, colorimetric	Validation Date: 7/4/75

1. Principle of the Method (Reference 11.1)

   1.1 1,1-Dimethylhydrazine is collected in a midget bubbler containing 0.1 M 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 1,1-dimethylhydrazine.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.506-2.22 mg/cu m, at an atmospheric temperature and pressure of 23°C and 760 mm Hg. The probable range of the method is 0.1-10 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 0.020 mg/cu m of 1,1-dimethylhydrazine can be determined in a 100-liter air sample based on a 0.025 absorbance using a 1-cm cell.

3. Interferences

   Potential interferences result from agents that can reduce the phosphomolybdic acid to form the blue oxide and hence, give an elevated reading--including stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide. Interferences from oxidation of the 1,1-dimethylhydrazine giving a diminished reading may occur with halogens and oxygen (especially in presence of Cu (I) ions). Other hydrazine derivatives will also interfere (elevating the reading) and hydrogen dioxide will possibly reoxidize the blue oxide giving a lower reading (References 11.2, 11.3, 11.4, and 11.5).

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.506-2.22 mg/cu m was 0.062. This value corresponds to a 0.062 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 11.6.

4.2 A collection efficiency of 0.991, standard deviation of 0.002, (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method. Thus, 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 A disadvantage of the method is the awkwardness in using midget bubblers for collecting samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

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

6. Apparatus

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

6.1.1 A glass, midget bubbler with a stem which has a fritted glass end and containing 10 ml of 0.1 M hydrochloric acid (Section 7.1). The fritted end should have porosity approximately equal to that of Corning EC (170-220 micron maximum pore diameter).

6.1.2 A pump suitable for sampling at least 1.0 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, large test tubes, and graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Collection Medium. 0.1 M hydrochloric acid. Fill a 1000-ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated hydrochloric acid, mix, and bring volume to the 1000-ml mark.

7.2 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.

7.3 1,1-Dimethylhydrazine, reagent grade.

7.4 1,1-Dimethylhydrazine standard solution. (500 mg of 1,1-dimethylhydrazine in 100 ml 0.1 M hydrochloric acid solution.)

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 10 ml of the 0.1 M hydrochloric acid (Section 7.1) 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 1.0 liter per minute or less. 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 2 ml 0.1 M hydrochloric acid. 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 Blank. With each batch of ten samples, submit one bubbler from the same lot of bubblers which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.4 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 three times with 2 ml 0.1 M hydrochloric acid and add rinses to the volumetric flask.

8.4.4 Add 10 ml phosphomolybdic acid solution to the volumetric flask. This may be carefully measured in a 10-ml graduated cylinder.

8.4.5 Bring solution to the 50-ml mark with 0.1 M hydrochloric acid.

8.4.6 Transfer solution to a large test tube and heat in a water bath at 98°C for 1 hour. Cool solution under running tap water.

8.4.7 Read at 730 nm within 30 minutes in the spectrophotometer against a blank prepared from the 0.1 M hydrochloric acid in the same fashion as the samples.

9. Calibration and Standards

9.1 To six 50-ml volumetric flasks, add 10 ml 0.1 M hydrochloric acid using a graduated cylinder.

9.2 Carefully pipet 10, 20, 30, 40, and 50 microliters of the standard solution into the flasks (Section 7.4). Process one flask as a blank.

9.3 Add to this mixture 10 ml of phosphomolybdic acid solution (Section 7.2) using a 10-ml graduated cylinder.

9.4 Bring the solution to the 50-ml mark with 0.1 M hydrochloric acid.

9.5 Transfer the solution to a large test tube and heat it in a water bath at 98°C for 1 hour. Cool the solution under running tap water.

9.6 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.

9.7 Read the blank in the sample cell, then read the samples at 730 nm.

9.8 Construct a calibration curve by plotting absorbance against milligrams of 1,1-dimethylhydrazine in the color developed solution.

10. Calculations

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

10.2 Determine from the calibration curve (Section 9.8) the mg of 1,1-dimethylhydrazine present in each sample.

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

$$\text{mg/cu m} = \frac{\text{mg 1,1-dimethylhydrazine (Section 10.2) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

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 Comprehensive Treatise on Inorganic and Theorectical Chemistry, J. W. Mellor (Longmans, N. Y.), 1948, Vol. VII and XI.

11.3 Inorganic Chemistry, Heslop and Robinson (Elsevier, N. Y.), 1967.

11.4 Advanced Inorganic Chemistry, Cotton and Wilkinson, (Interscience, N. Y.), 1966.

11.5 Inorganic Chemistry, T. Moeller (Wiley and Sons, N. Y.), 1963.

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

Analyte:	Ethylamine	Method No.:	S144
Matrix:	Air	Range:	7.41-31.8 mg/cu m
OSHA Standard:	10 ppm (18 mg/cu m)	Precision ($\overline{CV}_T$):	0.113
Procedure:	Adsorption on silica gel, desorption with aqueous sulfuric acid	Validation Date:	7/4/75

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 0.1 M sulfuric acid in an ultrasonic generator.

   1.3 An aliquot of the desorbed sample is made alkaline with 0.25 M sodium hydroxide, and an aliquot of the alkaline solution is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 7.41-31.8 mg/cu m at an atmospheric temperature and pressure of 25°C and 741 mm Hg, using a 30-liter sample. Under the conditions of sample size (30 liters) the probable range of this method is 1.8-54 mg/cu m. 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. 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 1.5 mg of the analyte when a test atmosphere of

31.8 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 240 minutes. Breakthrough did not occur at this time, i.e., no analyte was found in the backup section of the tube. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

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

3.4 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 7.41-31.8 mg/cu m was 0.113. This value corresponds to a standard deviation of 2.03 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2% 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 Section 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 compounds suspected to be present in the same sample by simply changing gas chromatographic conditions.

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 accurately (±5%) at the recommended flow rate (Reference No. 11.3).

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and 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 150 mg of silica gel, the backup section 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 1 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 (6-ft x 1/4-in glass) packed with 4% Carbowax 20M, plus 0.8% KOH on Carbopack B.

6.5 The GC inlet should have a removable glass liner.

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

6.7 Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

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

6.9 Pipets: 0.5 and 1.0-ml delivery type.

6.10 Ultrasonic bath capable of continuous operation for at least 3 hours.

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

7. Reagents

7.1 Eluent: 0.1 M sulfuric acid.

7.2 Aqueous sodium hydroxide, 0.25 M.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

7.6 Hydrion pH paper.

7.7 Aqueous ethylamine (33% by wt.), Matheson, Coleman and Bell.

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 backup 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 maximum sample size of 30 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 the pressure reading is not available the elevation should be recorded.

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

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

8.4 Analysis of Samples

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 or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Pipette 1.0 ml of 0.1 M sulfuric acid into each sample container. Stopper it securely and place it in an ultrasonic bath for three hours. Let the silica gel settle and pipette 0.5 ml of the supernatant solution into a second 2-ml glass sample container. Add 0.5 ml of 0.25 M sodium hydroxide solution and mix the resulting solution thoroughly. The pH of the resulting solution should be greater than 11 as indicated with pH paper. This solution should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.

2. 30 ml/min (50 psig) hydrogen gas flow to detector.

3. 300 ml/min (50 psig) air flow to detector.

4. 170°C injector temperature.

5. 210°C manifold temperature (detector).

6. 100°C column temperature.

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

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 technique. In this case five-microliter injections are recommended.

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 that 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 (150 mg) is measured into a 2.0-ml sample container. 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. A known amount of an aqueous solution containing 135 mg/ml of ethylamine is injected directly into the silica gel with a 10-microliter syringe, and the container is capped. The amount injected is equivalent to that present in a 30-liter sample at the selected level.

At least six tubes at each of the three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the silica gel. These six 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 a solution prepared from 1.0 ml of 0.1 M sulfuric acid and 1.0 ml 0.25 M sodium hydroxide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus the 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 0.1 M sulfuric acid basified with 1 ml 0.25 M sodium hydroxide. 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/ml versus peak area.

Note: Standard solutions should 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 weights, 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 0.1 M sulfuric acid basified with 1 ml 0.25 M sodium hydroxide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte 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.

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

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 Evan E. Campbell, Gerry O. Wood, and Robert G. Anderson, "Development of Air Sampling Techniques, Los Alamos Scientific Laboratory Progress Reports LA-5634-PR (June 1974), LA-5973-PR (July 1975), LA-6057-PR (September 1975).

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

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

N-Ethylmorpholine

Analyte:	N-Ethylmorpholine	Method No.: S146
Matrix:	Air	Range: 57-206 mg/cu m
OSHA Standard:	20 ppm (94 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.101
Procedure:	Adsorption on silica gel, desorption with aqueous sulfuric acid, GC	Validation Date: 7/4/75

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 0.1 M sulfuric acid in an ultrasonic generator.

   1.3 An aliquot of the desorbed sample is made alkaline with 0.25 M sodium hydroxide, and an aliquot of the alkaline solution is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 57-206 mg/cu m at an atmospheric temperature and pressure of 25°C and 741 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 10-300 mg/cu m. 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. 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 9.9 mg of the analyte when a test atmosphere of

206 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 240 minutes. Breakthrough did not occur at this time, i.e., no analyte was found in the backup section of the tube. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

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

3.4 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 57-206 mg/cu m was 0.101. This value corresponds to a standard deviation of 9.5 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.2% 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 Section 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 compounds suspected to be present in the same sample by simply changing gas chromatographic conditions.

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 accurately (±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 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 150 mg of silica gel, the backup section 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 1 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 (6-ft x 1/4-in glass) packed with 4% Carbowax 20M, plus 0.8% KOH on Carbopack B.

6.5 The GC inlet should have a removable glass liner.

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

6.7 Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

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

6.9 Pipets: 0.5 and 1.0-ml delivery type.

6.10 Ultrasonic bath capable of continuous operation for at least 3 hours.

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

7. Reagents

7.1 Eluent: 0.1 M sulfuric acid.

7.2 Aqueous sodium hydroxide, 0.25 M.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

7.6 Hydrion pH paper.

7.7 N-Ethylmorpholine, technical grade, Union Carbide Chemicals Co.

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 backup 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 10 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 $\pm$5%.

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

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

8.3.9 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 suspected compound should be submitted to the laboratory in glass containers with Teflon-lined caps. These liquid bulk samples 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 or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Pipette 1.0 ml of 0.1 M sulfuric acid into each sample container. Stopper it securely and place it in an ultrasonic bath for three hours. Let the silica gel settle and pipette 0.5 ml of the supernatant solution into a second 2-ml glass sample container. Add 0.5 ml of 0.25 M sodium hydroxide solution and mix the resulting solution thoroughly. The pH of the resulting solution should be greater than 11 as indicated with pH paper. This solution should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.

2. 30 ml/min (50 psig) hydrogen gas flow to detector.

3. 300 ml/min (50 psig) air flow to detector.

4. 200°C injector temperature.

5. 210°C manifold temperature (detector).

6. 180°C column temperature.

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

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 technique. In this case five-microliter injections are recommended.

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 that 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 (150 mg) is measured into a 2.0-ml sample container. 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. A known amount of an aqueous solution containing 235 mg/ml of N-ethylmorpholine is injected directly into the silica gel with a 10-microliter syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level.

At least six tubes at each of the three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the silica gel. These six 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 a solution prepared from 1.0 ml 0.1 M sulfuric acid and 1.0 ml 0.25 M sodium hydroxide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus the 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 0.1 M sulfuric acid basified with 1 ml 0.25 M sodium hydroxide. 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 concentrations in mg/ml versus peak area.

Note: Standard solutions should 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 weights, 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 0.1 M sulfuric acid basified with 1 ml 0.25 M sodium hydroxide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte 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.

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

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 Evan E. Campbell, Gerry O. Wood, and Robert G. Anderson, "Development of Air Sampling Techniques, Los Alamos Scientific Laboratory Progress Reports LA-5634-PR (June 1974), LA-5973-PR (July 1975), LA-6057-PR (September 1975).

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

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

Isopropylamine

Analyte:	Isopropylamine	Method No.:	S147
Matrix:	Air	Range:	8.9-21.5 mg/cu m
OSHA Standard:	5 ppm (12 mg/cu m)	Precision ($\overline{CV}_T$):	0.067
Procedure:	Bubbler collection in dilute sulfuric acid, GC analysis of the collected samples after basification with sodium hydroxide	Validation Date:	7/4/75

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 0.05 M sulfuric acid to trap the organic vapors present.

   1.2 The resulting solution is made alkaline with 4 M sodium hydroxide.

   1.3 An aliquot of 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 8.9-21.5 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 1-35 mg/cu m.

3. Interferences

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.9-21.5 mg/cu m was 0.067. This value corresponds to a 0.8 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 was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no significant bias is introduced in the sample collection step. There is no apparent bias in the analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

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

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 sampling at least 1 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 Gas chromatograph equipped with a hydrogen flame ionization detector.

6.3 Column (6-ft long X 1/4-in O.D. glass) packed with 4% Carbowax 20 M and 0.8% KOH on Carbopak B. A 3-in Ascarite "precolumn" is inserted at the inlet end of the column and is separated from the column packing with a plug of glass wool. The Ascarite "precolumn" should be checked periodically for salt buildup. The column should be baked out at 200°C at the end of each day, and the Ascarite should be changed at least once a month. (Reference 11.1)

6.4 The GC inlet should have a removable glass liner that can be cleaned.

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

6.6 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.

6.7 Volumetric flasks: convenient sizes for making solutions.

6.8 Pipets: 10-ml or other convenient sizes.

7. Reagents

7.1 Isopropylamine, reagent grade.

7.2 Collection medium, 0.05 M sulfuric acid.

7.3 Sodium hydroxide, 4 M (160 g of sodium hydroxide in distilled water, diluted to a final volume of 1 liter).

7.4 Purified nitrogen.

7.5 Purified hydrogen.

7.6 Filtered compressed air.

7.7 Hydrion pH paper.

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 10 ml of the collection medium (Section 7.2) into each midget bubbler, and mark the liquid level.

8.3.2 Connect the midget bubbler with a 5-cm glass splashover 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 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 or less. A sample size of 100 liters is recommended.

8.3.4 After sampling, the bubbler stem may be removed and cleaned. If necessary, bring the volume of each sample to the 10-ml mark with 0.05 M sulfuric acid. 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 0.05 M sulfuric acid, 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 With each batch of ten samples, submit one bubbler from the same lot of bubblers 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.

8.4 Analysis of Samples

8.4.1 The sample in each bubbler is analyzed separately.

8.4.2 Add 1 ml of 4 M sodium hydroxide to the sample and mix the solution thoroughly. The pH of the resulting solution should be greater than 10 as indicated with pH paper. The total volume of the solution should be 12 ml and should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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. 205°C injector temperature
5. 270°C manifold temperature (detector)
6. 110°C column temperature

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

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 means of area measurement, and preliminary results are read from a standard curve prepared as discussed below in Section 9.

8.5 Standard Solutions

8.5.1 Procedure for preparing standard solutions. Standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of isopropylamine in water (300 mg/ml) into 11 ml of 0.05 M sulfuric acid in a bubbler. The amount introduced is equivalent to that present in a 100-liter air sample. The standards are made alkaline with 1.0 ml of 4 M sodium hydroxide. The solution should be checked with pH paper to make sure that its pH is greater than 10. 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.

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

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

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

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

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 Di Corcia, Antonio and Roberto Samperi, Gas Chromatographic Determination at the Parts-per-Million Level of Aliphatic Amines in Aqueous Solution," Anal. Chem., 46, No. 8, July 1974, 977-981.

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

Monomethyl Hydrazine

Analyte:	Monomethyl Hydrazine	Method No.:	S149
Matrix:	Air	Range:	0.169-0.78 mg/cu m
OSHA Standard:	0.2 ppm (0.35 mg/cu m) - Ceiling	Precision ($\overline{CV}_T$):	0.106
Procedure:	Bubbler collection, colorimetric	Validation Date:	7/4/75

1. Principle of the Method (Reference 11.1)

   1.1 Monomethyl hydrazine is collected in a midget bubbler containing 0.1 M 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 monomethyl hydrazine.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.169-0.78 mg/cu m, at an atmospheric temperature and pressure of 23°C and 760 mm Hg. The probable range of the method is 0.035-1.05 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 0.035 mg/cu m of monomethyl hydrazine can be determined in a 20-liter air sample based on a 0.025 absorbance using a 5-cm cell.

3. Interferences

   Potential interferences result from agents that can reduce the phosphomolybdic acid to form the blue oxide and hence, give an elevated reading--including stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide. Interferences from oxidation of the monomethyl hydrazine giving a diminished reading may occur with halogens and oxygen (especially in presence of Cu (I) ions). Other hydrazine derivatives will also interfere (elevating the reading) and hydrogen dioxide will possibly reoxidize the blue oxide giving a lower reading (References 11.2, 11.3, 11.4, and 11.5).

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.169-0.78 mg/cu m was 0.106. This value corresponds to a 0.037 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 11.6.

4.2 A collection efficiency of 0.965, standard deviation of 0.022, (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

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

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

5.4 Monomethyl hydrazine is slowly air-oxidized and is difficult to maintain known purity. Therefore, all analytical work is done using a stable salt such as the sulfate of monomethyl hydrazine.

6. Apparatus

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

6.1.1 A glass, midget bubbler with a stem which has a fritted glass end and containing 15 ml of 0.1 M hydrochloric acid (Section 7.1). The fritted end should have porosity approximately equal to that of Corning EC (170-220 micron maximum pore diameter).

6.1.2 A pump suitable for sampling at least 1.5 liter per minute for 15 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, 5-cm path length.

6.4 Assorted laboratory glassware -- pipets, volumetric flasks, large test tubes, and graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Collection Medium. 0.1 M hydrochloric acid. Fill a 1000-ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated hydrochloric acid, mix, and bring volume to the 1000-ml mark.

7.2 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.

7.3 Methylhydrazine sulfate.

7.4 Methylhydrazine sulfate, standard solution. Weigh accurately 0.1000 gram methylhydrazine sulfate in a 100-ml volumetric flask and fill to the mark with 0.1 M hydrochloric acid.

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 M hydrochloric acid (Section 7.1) 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 1.5 liter per minute for 15 minutes.

8.3.4 After sampling, the bubbler stems are lifted out of the bubbler bottom and rinsed with approximately 1 ml 0.1 M hydrochloric acid. 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 Blank. With each batch of ten samples, submit one bubbler from the same lot of bubblers which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.4 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 with 1 ml 0.1 M hydrochloric acid and add rinse to the volumetric flask.

8.4.4 Add 7.5 ml phosphomolybdic acid solution to the volumetric flask. This may be carefully measured in a 10-ml graduated cylinder.

8.4.5 Bring solution to the 25-ml mark with 0.1 M hydrochloric acid.

8.4.6 Transfer solution to a large test tube and heat in a water bath at 87°C for 50 minutes. Cool solution under running tap water.

8.4.7 Read at 730 nm within 30 minutes in the spectrophotometer against a blank prepared from the 0.1 M hydrochloric acid in the same fashion as the samples.

9. Calibration and Standards

9.1 To five 25-ml volumetric flasks, add 15 ml 0.1 M hydrochloric acid using a graduated cylinder.

9.2 Carefully pipet 10, 25, 50, and 100 microliters of the standard solution into the flasks (Section 7.4). Process one flask as a blank.

9.3 Add to this mixture 7.5 ml of phosphomolybdic acid solution (Section 7.2) using a 10-ml graduated cylinder.

9.4 Bring the solution to the 25-ml mark with 0.1 M hydrochloric acid.

9.5 Transfer the solution to a large test tube and heat it in a water bath at 87°C for 50 minutes. Cool the solution under running tap water.

9.6 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.

9.7 Read the blank in the sample cell, then read the samples at 730 nm.

9.8 Construct a calibration curve by plotting absorbance against milligrams of monomethyl hydrazine in the color developed solution. Since the calibration curve is made using aliquots of methylhydrazine sulfate, the weight of monomethyl hydrazine must be calculated.

$$\text{mg, methyl hydrazine} = \text{mg methylhydrazine sulfate} \times \frac{46.07}{144} \times \frac{\text{ml standard}}{100 \text{ ml}}$$

where:

46.07 = molecular weight of methyl hydrazine

144 = molecular weight of methylhydrazine sulfate

10. Calculations

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

10.2 Determine from the calibration curve (Section 9.8) the mg of monomethyl hydrazine present in each sample.

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

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

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 Comprehensive Treatise on Inorganic and Theoretical Chemistry, J. W. Mellor (Longmans, N.Y.), 1948, Vols. VII and XI.

11.3 Inorganic Chemistry, Heslop and Robinson (Elsevier, N.Y.), 1967.

11.4 Advanced Inorganic Chemistry, Cotton and Wilkinson (Interscience, N.Y.), 1966.

11.5 Inorganic Chemistry, T. Moeller (Wiley & Sons, N.Y.). 1963.

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

Morpholine

Analyte:	Morpholine	Method No.:	S150
Matrix:	Air	Range:	28.5-108.4 mg/cu m
OSHA Standard:	20 ppm (70 mg/cu m) - skin	Precision ($\overline{CV}_T$):	0.057
Procedure:	Adsorption on silica gel, desorption with 0.05 M sulfuric acid, GC	Validation Date:	7/4/75

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 0.05 M sulfuric acid.

   1.3 An aliquot of the desorbed sample is transferred to another small stoppered sample container and made alkaline with 1.2 M sodium hydroxide.

   1.4 An aliquot of the alkaline solution is injected into a gas chromatograph.

   1.5 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 28.5-108.4 mg/cu m at an atmospheric temperature and pressure of 23°C and 763 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 7-210 mg/cu m. 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 6.0 mg of analyte when a test atmosphere containing 135 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. At that time the concentration of morpholine in the effluent was less than 5% of the influent. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 28.5-108.4 mg/cu m was 0.057. This value corresponds to a 4.0 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collection medium. Thus, no correction for collection efficiency was necessary, and it was assumed that no significant bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which a desorption efficiency 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. 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.

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 ± 5% at the recommended flow rate. Reference 11.1.

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 (4-ft long by 1/4-in stainless steel) packed with 80/100 mesh Chromosorb 103. A 3-in Ascarite "precolumn" is inserted at the inlet end of the column and is separated from the Chromosorb 103 column packing by a plug of glass wool. The Ascarite "precolumn" should be checked periodically for salt buildup. The column should be baked out at 200°C at the end of each day, and the Ascarite "precolumn" should be changed at least once a month. (Reference 11.2)

6.5 The GC inlet should have a removable glass liner that can be cleaned.

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

6.7 Two-milliliter sample containers with glass stoppers or Teflon-lined caps.

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 Sulfuric acid, 0.05 M.

7.2 Sodium Hydroxide, 1.2 M.

7.3 Morpholine, reagent grade.

7.4 n-Hexane, reagent grade.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

7.7 Purified nitrogen.

7.8 pH paper - Hydrion.

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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

8.3.9 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 0.05 M sulfuric acid is pipetted into each sample container. The sample is desorbed for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. Transfer a 0.5-ml aliquot of the desorbed sample to a new vial, and add 50 microliters of 1.2 M sodium hydroxide to make the solution alkaline. Mix the solution well. The pH of the resulting solution should

be greater than 10 as indicated with pH paper. This solution should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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. 250°C injector temperature
5. 280°C manifold temperature (detector)
6. 300°C column temperature

The glass inlet liner should be removed from the gas chromatograph and cleaned with water and acetone rinses at the end of each day. Reinsert the glass inlet into the injection port, and let it bake out overnight.

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 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 morpholine containing 350 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 a solution prepared from 1.0 ml of 0.05 M sulfuric acid and 100 microliters of 1.2 M sodium hydroxide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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 10.1 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml 0.05 M sulfuric acid basified with 100 microliters of 1.2 M sodium hydroxide, because samples are desorbed in this amount of eluent. The density of the analyte is used to calculate mgs from 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 0.05 M sulfuric acid basified with 100 microliters of 1.2 M sodium hydroxide and the volume of sample injected is identical to the volume of the standards injected.

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

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

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.

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

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 Evan E. Campbell, Gerry O. Wood, and Robert G. Anderson, "Development of Air Sampling Techniques, Los Alamos Scientific Laboratory Progress Reports LA-5634-PR (June 1974), LA-5973-PR (July 1975), LA-6057-PR (September 1975).

11.2 C. E. Andre and A. R. Mosier, "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines," Analytical Chemistry 45, 1971 - 1973 (1973).

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

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

Triethylamine

Analyte:	Triethylamine	Method No.: S152
Matrix:	Air	Range: 50-193 mg/cu m
OSHA Standard:	25 ppm (100 mg/cu m)	Precision ($\bar{CV}_T$): 0.064
Procedure:	Bubbler collection, GC analysis after basification	Validation Date: 7/4/75

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 0.05 M sulfuric acid to trap the organic vapors present.

   1.2 The resulting solution is made alkaline with 4 M sodium hydroxide.

   1.3 An aliquot of 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 50-193 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 10-300 mg/cu m.

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 50-193 mg/cu m was 0.064. This value corresponds to a 6.4 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 5.6% 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.

A collection efficiency of 1.00 was determined for the collecting medium. Therefore, no recovery correction should be applied to the final result in Section 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 A major disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the adsorbing solution during sampling may occur which will result in loss of the sample.

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

6. Apparatus

6.1 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 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 Gas chromatograph equipped with a hydrogen flame ionization detector.

6.3 Column (6-ft long X 1/4-in O.D. glass) packed with 4% Carbowax 20 M and 0.8% KOH on Carbopak B. A 15-cm Ascarite "precolumn" is inserted at the inlet end of the column and is separated from the column packing with a plug of glass wool. The Ascarite "precolumn" should be checked periodically. The column should be baked out at 200°C at the end of each day, and the Ascarite should be changed at least once a month. (Reference 11.1)

6.4 The GC inlet should have a removable glass liner that can be cleaned.

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

6.6 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.

6.7 Volumetric flasks: convenient sizes for making solutions.

6.8 Pipets: 10 ml or other convenient sizes.

7. Reagents

7.1 Triethylamine, reagent grade.

7.2 Collection medium, 0.05 M sulfuric acid.

7.3 Sodium hydroxide, 4 M (160 g of sodium hydroxide in distilled water, diluted to a final volume of 1 liter).

7.4 Purified nitrogen.

7.5 Purified hydrogen.

7.6 Filtered compressed air.

7.7 Hydrion pH paper.

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 Pipet 10 ml of the collection medium (Section 7.2) into each midget bubbler, and mark the liquid level.

8.3.2 Connect the midget bubbler with a 5-cm glass splashover 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 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 or less. A sample size of 100 liters is recommended.

8.3.4 After sampling, the bubbler stem may be removed and cleaned. If necessary, bring the volume of each sample to the 10-ml mark with 0.05 M sulfuric acid. 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 approximately 1 ml of 0.05 M sulfuric acid, 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 With each batch of ten samples, submit one bubbler from the same lot of bubblers 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.

8.4 Analysis of Samples

8.4.1 The sample in each bubbler is analyzed separately.

8.4.2 Add 1 ml of 4 M sodium hydroxide to the sample and mix the solution thoroughly. The pH of the resulting solution should be greater than 10 as indicated with pH paper. The total volume of the solution should be 12 ml * and should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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. 215°C injector temperature
5. 250°C manifold temperature (detector)
6. 135°C column temperature

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

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.

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* If the final volume of the solution is greater than 12 ml, an appropriate calculation adjustment must be made. If the volume is less than 12 ml, make it up to 12 ml with base.

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 means of area measurement, and preliminary results are read from a standard curve prepared as discussed below in Section 9.

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.

mg = mg sample - mg blank

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

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

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

10.4 Another method of expressing concentration is ppm.

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

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 Di Corcia, Antonio and Roberto Samperi, "Gas Chromatographic Determination at the Parts-per-Million Level of Aliphatic Amines in Aqueous Solution," Anal. Chem., 46, No. 8, July 1974, 977-981.

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

Monomethyl Aniline

Analyte:	Monomethyl Aniline	Method No.: S153
Matrix:	Air	Range: 4.38-17.52 mg/cu m
OSHA Standard:	2 ppm (9 mg/cu m)-skin	Precision (CV_T): 0.089
Procedure:	Bubbler collection in dilute sulfuric acid, GC analysis of the collected samples after basification with sodium hydroxide	Validation Date: 7/4/75

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 0.05 M sulfuric acid to trap the organic vapors present.

   1.2 The resulting solution is made alkaline with 4 M sodium hydroxide.

   1.3 An aliquot of 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 4.38-17.52 mg/cu m at an atmospheric temperature and pressure of 22°C and 762 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 1-30 mg/cu m.

3. Interferences

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 4.38-17.52 mg/cu m was 0.089. This value corresponds to a 0.8 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 3.9% 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.

A collection efficiency of 1.00 was determined for the collecting medium. Therefore, no recovery correction should be applied to the final result in Section 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 A major disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the adsorbing solution during sampling may occur which will result in loss of the sample.

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 sampling at least 1 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 Gas chromatograph equipped with a hydrogen flame ionization detector.

6.3 Column (2-ft long X 1/8-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 103. An Ascarite precolumn may be used if necessary to prevent contamination of the column packing with salt.

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: 10-ml or other convenient sizes.

7. Reagents

7.1 Monomethyl Aniline (N-Methylaniline), reagent grade.

7.2 Collection medium, 0.05 M sulfuric acid.

7.3 Sodium hydroxide, 4 M (160 g of sodium hydroxide in distilled water, diluted to a final volume of 1 liter).

7.4 Purified nitrogen.

7.5 Purified hydrogen.

7.6 Filtered compressed air.

7.7 Hydrion pH paper.

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 10 ml of the collection medium (Section 7.2) into each midget bubbler, and mark the liquid level.

8.3.2 Connect the midget bubbler with a 5-cm glass splashover 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 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 or less. A sample size of 100 liters is recommended.

8 3.4 After sampling, the bubbler stem may be removed and cleaned. If necessary, bring the volume of each sample to the 10-ml mark with 0.05 M sulfuric acid. 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 0.05 M sulfuric acid, 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 With each batch of ten samples, submit one bubbler from the same lot of bubblers 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.

8.4 Analysis of Samples

8.4.1 The sample in each bubbler is analyzed separately.

8.4.2 Add 1 ml of 4 M sodium hydroxide to the sample and mix the solution thoroughly. The pH of the resulting solution should be greater than 10 as indicated with pH paper. The total volume of the solution should be 12 ml and should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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. 245°C injector temperature
5. 275°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 means of area measurement, and preliminary results are read from a standard curve prepared as discussed below in Section 9.

8.5 Standard Solutions

8.5.1 Procedure for preparing standard solutions. Standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of monomethyl aniline in benzene (219 mg/ml) into 11 ml of 0.05 M sulfuric acid in a bubbler. The amount introduced is equivalent to that present in a 100-liter air sample. The standards are made alkaline with 1.0 ml of 4 M sodium hydroxide. The solution should be checked with pH paper to make sure that its pH is greater than 10. 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.

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

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

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

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

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 Di Corcia, Antonio and Roberto Samperi, "Gas Chromatographic Determination at the Parts-per-Million Level of Aliphatic Amines in Aqueous Solution," Anal. Chem., 46, No. 8, July 1974, 977-981.

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

Analyte:	Tetramethyl Succinonitrile	Method No.: S155
Matrix:	Air	Range: 1.80-8.20 mg/cu m
OSHA Standard:	0.5 ppm (3 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.075
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 7/4/75

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 1.80-8.20 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 55-liter sample. Under the conditions of sample size (55 liters) the probable useful range of this method is 0.5-10 mg/cu m. 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 tetramethyl succinonitrile and other substances in the air. The first section of the charcoal tube was found to hold at least 0.78 mg of tetramethyl succinonitrile when a test atmosphere containing 3.63 mg/cu m of tetramethyl succinonitrile in air was sampled at 0.90 liter per minute for 240 minutes; breakthrough was not observed at this time since no tetramethyl succinonitrile was detected in the backup section of

the charcoal tube. (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. Interferences

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

3.3 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 1.80-8.20 mg/cu m was 0.075. This value corresponds to a 0.23 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 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which a desorption efficiency 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. 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.

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 ±5% at the recommended flow rate.

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 (6-ft X 1/4-in I.D. stainless steel) packed with 5% SE-30 on 80/100 mesh Chromosorb W DMCS.

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 Tetramethyl Succinonitrile, reagent grade.

7.3 Hexane, reagent grade.

7.4 Acetone, reagent grade.

7.5 Purified nitrogen.

7.6 Prepurified 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 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 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 $\pm 5\%$.

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 With each batch of ten samples submit one tube from the same lot of tubes 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.

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

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file 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. 230°C injector temperature
5. 255°C manifold temperature (detector)
6. 90°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 a 20% (V/V) acetone-hexane solution of tetramethyl succinonitrile containing 34.75 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 50-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

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

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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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 Cortract No. CDC-99-74-45.

Acrylonitrile

Analyte:	Acrylonitrile	Method No.: S156
Matrix:	Air	Range: 17.5-70.0 mg/cu m
OSHA Standard:	20 ppm (45 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.073
Procedure:	Adsorption on charcoal, desorption with methanol, GC	Validation Date: 7/4/75

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 methanol.

   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 17.5-70.0 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 4.5-135 mg/cu m. 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 acrylonitrile and other substances in the air. The first section of the charcoal tube was found to hold at least 3.97 mg of acrylonitrile when a test atmosphere containing 92.0 mg/cu m of acrylonitrile in air was sampled at 0.18 liter per minute for 240 minutes; at that time the concentration of acrylonitrile 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. Interferences

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

3.3 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 17.5-70.0 mg/cu m was 0.073. This value corresponds to a 3.3 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 6.0% 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 Section 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.

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 ±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 (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 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: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality methanol.

7.2 Acrylonitrile, reagent grade.

7.3 Hexane, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 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 ±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 With each batch of ten samples submit one tube from the same lot of tubes 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.

8.3.9 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 methanol 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. 235°C injector temperature
5. 255°C manifold temperature (detector)
6. 155°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 (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 acrylonitrile containing 0.239 g/ml is injected directly into the activated charcoal 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 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 methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

The desorption efficiency is dependent on the amount of 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 methanol, because samples are desorbed in this amount of methanol. 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 methanol and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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.

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.

$$\text{equivalent mg of phenylhydrazine} = \text{mg phenylhydrazine·HCl weighed out in standard} \times \frac{108.14}{144.6} \times \frac{\text{ml standard}}{100\ \text{ml}}$$

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.

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 ±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 of 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 [illegible] 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 should be made. No more than a 3% difference in area should 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 [illegible].

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 by each 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

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

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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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.

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, 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 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 ±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 $\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 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.** A 100-mg 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. The 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 a rubber cap. A known amount of hexane solution of xylidine, usually 125 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with a cap. 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

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

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:

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 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-5339-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.

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 ±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 $\pm 5\%$.

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 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

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

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.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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.

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 ± 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 thr gh 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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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 ±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 ±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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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.

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 ±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 $\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 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 reporducitility 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

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

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:

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.

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

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 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.

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 $\pm$ 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 ($FeCl_3 \cdot 6H_2O$) 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.

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

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.

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 $\pm$ 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 $\pm$ 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 interferring 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 hyirochloric 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 ±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 within 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 $Ba(ClO_4)_2$ is calculated as follows:

$$M_{Ba(ClO_4)_2} = \frac{ml_{Na_2SO_4} \times M_{Na_2SO_4}}{ml_{Ba(ClO_4)_2}}$$

where:

$ml_{Na_2SO_4}$ = ml Na_2SO_4 solution needed to titrate $Ba(ClO_4)_2$

$M_{Na_2SO_4}$ = Molarity of Na_2SO_4

$ml_{Ba(ClO_4)_2}$ = ml $Ba(ClO_4)_2$ used

The molarity of $Ba(ClO_4)_2$ should be checked periodically.

10. Calculations

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

$$H_2SO_4 + Ba(ClO_4)_2 \rightarrow BaSO_4\downarrow + 2HClO_4$$

10.2 The mg of H_2SO_4 can be calculated as follows:

$$mg\ H_2SO_4 = M_{Ba(ClO_4)_2} \times ml_{Ba(ClO_4)_2} \times 98$$

where:

$M_{Ba(ClO_4)_2}$ = Molarity of $Ba(ClO_4)_2$ solution.

$ml_{Ba(ClO_4)_2}$ = ml of $Ba(ClO_4)_2$ solution needed to titrate the sample.

98 = Molecular weight of H_2SO_4.

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

mg = mg sample - mg blank

where:

mg sample = mg found in sample filter

mg blank = 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.

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

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. Rundechau, 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.

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 interferring 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..).

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:

mg sample = mg found in sample bubbler

mg blank = 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.

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

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. Reference

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 $\pm$ 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 $\pm$ 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 $\pm$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:

mg sample = mg found in sample bubbler

mg blank = 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.

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

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.

2-Hexanone
(Methyl Butyl Ketone)

Analyte:	2-Hexanone	Method No.:	S178
Matrix:	Air	Range:	188-790 mg/cu m
OSHA Standard:	100 ppm (410 mg/cu m)	Precision ($\overline{CV}_T$):	0.053
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	8/29/75

1. Principle of the Method

   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 from injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 188-790 mg/cu m at an atmospheric temperature and pressure of 27.7°C and 767 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 40-1200 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 35 mg of analyte when a test atmosphere containing 790 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.

(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 as 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 188-790 mg/cu m was 0.053. This value corresponds to a 22-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 0.5% 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.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 80/100 mesh Chromosort W AW-DMCS.

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 type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 2-Hexanone, reagent grade

7.3 Decane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 of 10 liters is recommended. Sample at a rate 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 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 80°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

11.1 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.

Phthalic Anhydride

Analyte:	Phthalic Anhydride	Method No.:	S179
Matrix:	Air	Range:	5.5-28 mg/cu m
OSHA Standard:	2 ppm (12 mg/cu m)	Precision ($\overline{CV}_T$):	0.089
Procedure:	Filter collection, extraction and hydrolysis with aqueous ammonia, HPLC	Validation Date:	[illegible]

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and treated with aqueous ammonia; the anhydride is hydrolyzed to the acid and extracted in the acid form.

1.3 An aliquot of the sample is injected into a high performance liquid chromatograph (HPLC) equipped with a 254 nm UV detector.

1.4 The area of the resulting sample peak is used as a measure of analyte concentration by comparison with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 5.5-28 mg/cu m at an atmospheric temperature and pressure of 22°C and 765 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 1-36 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3.6 mg sample based on the dilution and sample aliquots specified in this method. (Refer to Section 8.4.)

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 average collection efficiency for phthalic anhydride aerosol is 96% when sampled for 70 minutes at 1.5 liters per minute from test atmospheres containing 17-50 mg/cu m.

3. Interference

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 5.5-28 mg/cu m was 0.089. This value corresponds to a standard deviation of 1.1 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 95.6% was determined for the collecting medium; thus, no significant bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery for the filters was 98.9%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

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

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

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

6.3 High Pressure Liquid Chromatograph equipped with a 254 nm UV detector.

6.4 Column (25 cm x 4.6 mm I.D. stainless steel) packed with Partisil[tm] 10.

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

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

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

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions and sample dilutions.

6.9 Pipets: 1,5-milliliter and other convenient sizes for making standard solutions and sample dilutions.

7. Reagents

7.1 Phthalic anhydride, reagent grade.

7.2 Ethylacetate, Spectroquality.

7.3 [illegible]chanol, Spectroquality.

7.4 Glacial Acetic acid.

7.5 Acetic acid in methanol, 10%. Prepare by diluting 10 ml of glacial acetic acid to 100 ml with methanol.

7.6 Ammonium hydroxide, 0.2 N. Add 14 ml of concentrated ammonia (15 N) to distilled water and dilute to 1.0 liter.

7.7 Chromatographic Solvent System. Mix together glacial acetic acid, methanol, and methylene chloride in the proportion - 10 ml, 20 ml and 220 ml, respectively.

7.8 Acetone, Spectroquality.

7.9 Isopropyl alcohol, Spectroquality.

8. Procedure

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

8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and shipping of samples.

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

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

8.3.3 A sample size of 100 liters is recommended. Sample at a flow rate of 1.5 liter per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

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

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

8.3.6 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet ends.

8.3.7 Carefully record sample identity and all relevant sample data.

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

8.3.9 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder. Carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to the jar.

2. Pipet 5-ml of 0.2 N ammonium hydroxide into the jar and cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted. Let stand for at least one hour, with occassional agitation, to effect complete hydrolysis and extraction.

3. Transfer, with a pipet, 1.0 ml of the above extract into a 10-ml volumetric flask. Acidify with 2 ml of the 10% acetic acid/methanol solution and dilute to volume with ethylacetate. It should be noted that this solution of phthalic acid is not stable beyond a normal working day and should accordingly be prepared as needed.

8.4.2 Analysis by high pressure liquid chromatograph. The chromatographic solvent system used is described in Section 7.7. The typical operating conditions for the liquid chromatograph are:

1. 0.8 ml/min solvent flow rate

2. Ambient column temperature

3. 500-800 psi system pressure

8.4.3 Injection. The first step in the analysis is the injection of the sample into the liquid chromatograph. A 20 µl-sample aliquot is recommended for this analysis. The sample may be injected either by using a high pressure syringe or by filling a fixed volume sample loop provided that reproducibility requirements are satisfied. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the

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

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm$5%.

The spiking solution* is prepared as follows. Transfer 0.3400 g of phthalic anhydride into a 25 ml volumetric. Add 2.5 ml of acetone to dissolve analyte and gradually add isopropyl alcohol. Phthalic anhydride might initially crystallize out during the isopropyl alcohol addition but the crystals will readily go into solution upon addition of more alcohol and ultrasonic agitation. Dilute to volume with isopropyl alcohol. An amount of the analyte equivalent to that present in a 100-liter sample at the selected level should be used for the extraction studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) are spiked. A parallel blank filter is also prepared except that no sample is added to it. All filters are then extracted and analyzed as described in Section 8.4. The recovery values obtained in validating this method were at least 99% and as such no correction factor has been used in the determination of the "true" values.

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

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

*The spiking solution is not stable. The phthalic anhydride is gradually converted to the half-acid/half-ester by the isopropyl alcohol. Unfortunately, no other solvent system was found which satisfies the requirements for phthalic anhydride solubility and cellulose membrane filter compatibility. Limited studies indicate that the anhydride content of this solution decreases to 95% within the first hour and 90% by the second hour and must therefore be used within the first hour to minimize errors.

9. Calibration and Standards

9.1 Phthalic anhydride stock solution*, 10 µg/µl. Dissolve 1.000 g of phthalic anhydride in 100 ml of ethylacetate. This solution is stable for at least one week.

9.2 From the 10 µg/µl stock standard solution, prepare at least 6 working standards to cover the concentration range of 100-600 µg/10 ml. Transfer 10 to 60 µl aliquots of the stock standard into 10-ml volumetric flasks and treat with 1.0 ml of 0.2 N ammonium hydroxide solution. Let stand for at least 15 minutes, acidify with 2 ml of 10% acetic acid/methanol, and dilute to volume with ethylacetate.

9.3 These series of standards are analyzed under the same HPLC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

NOTE: To minimize effect of variations in LC conditions and detector response due to sample cell conditions, frequent standardization should be practiced.

10. Calculations

10.1 Read the concentration, in µg/10 ml, corresponding to the peak area from the standard curve. No volume corrections for sample aliquots analyzed are needed, because the standard curve is based on µg per 10.0 ml and the volume of sample injected is identical to the volume of the standards injected. However, this concentration found must be multiplied by the dilution factor 5 to obtain the total µg found.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

*This solution should not be used for spiking because the ethylacetate attacks the filter leading to very low recoveries of anhydride.

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

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

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

where:

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

11. Reference

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

Tin, Inorganic Compounds Except Oxides

Analyte:	Tin	Method No.:	S183
Matrix:	Air	Range:	0.939-4.32 mg/cu m
OSHA Standard:	2 mg/cu m	Precision ($\overline{CV}_T$):	0.055
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

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

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 Samples are ashed using nitric and sulfuric acids to destroy the filter and any organic material, and the tin, including tin inorganic compounds, is then solubilized in dilute hydrochloric acid.

1.3 The solutions of samples and standards are aspirated into the reducing air-acetylene flame of an atomic absorption spectrophotometer (AAS). An electrodeless discharge for tin is used.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.939-4.32 mg/cu m using a 250-liter sample at an atmospheric temperature and pressure of 22.7°C and 747 mm Hg. Under the conditions of sample size (250 liters), the working range of the method is estimated to be 0.5-6 mg/cu m.

2.2 The sensitivity of this method using the 5-ml final solution volume is 10 micrograms of tin (2 micrograms/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

Any tin compound which is collected on the filter will be measured.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.939-4.32 mg/cu m is 0.055. This value corresponds to a 0.11 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There is also no 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 quick, instrumental method.

5.2 This method is not specific for inorganic tin compounds. Any tin compound which is collected on the MCEF filter will be measured and will be an interference.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

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

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tin electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

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

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1,5, 10 ml.

6.4.3 Volumetric flasks of appropriate sizes.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

6.6 Muffle furnace capable of controlling temperature at 200°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Stannous chloride, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 Dilute hydrochloric acid (10 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water).

7.5 Concentrated hydrochloric acid.

7.6 Concentrated sulfuric acid.

7.7 Commercially prepared aqueous standard stock solutions; 1000 micrograms/ml of tin.

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and distilled water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 250 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 1 ml of concentrated sulfuric acid and 5 ml of concentrated nitric acid. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until fumes of sulfuric acid appear. If any black suspension remains, add a few drops of concentrated nitric acid and fume again until a clear solution is obtained. Cool the beaker. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker. Return the beaker to the hot plate and heat until all the sulfuric acid fumes disappear. To remove the last traces of sulfuric acid, heat the beaker in a muffle furnace at a temperature of 200°C for about 1 hour.

8.4.3 Cool each beaker and dissolve residues in 5 ml (pipetted) dilute hydrochloric acid (Section 7.4). The addition of the dilute hydrochloric acid must be quantitative. Swirl to wash down sides of the beaker and mix thoroughly.

8.4.4 Aspirate the solutions into a reducing air-acetylene flame and record the absorbance at 224.6 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response.

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

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

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the levels (0.5X, 1X, and 2X the OSHA standard). Appropriate amounts of stannous chloride are dissolved in 25 ml concentrated HCl and diluted to 250 ml with distilled water to represent each of the three levels. Three sets of six filters are spiked with appropriate volumes of each standard solution for each

of the three levels. This corresponds to the amount of tin collected in a 250-liter sample at the 0.5X, 1X, and 2X levels, respectively.

Allow the filters to dry and place each filter in a cassette filter holder, and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except than no sample is added to it.

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

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

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 150 to 1500 micrograms/5 ml from the 1000 micrograms/ml stock tin standard solution. Make all standard solutions in dilute hydrochloric acid and prepare fresh daily.

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

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram per 5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/5 ml.

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

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

where:

µg sample = µg found in sample filter

µg blank = µg found in blank filter

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

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

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Zirconium Compounds (as Zr)

Analyte:	Zirconium	Method No.:	S185
Matrix:	Air	Range:	2.1-9.0 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.053
Procedure:	Filter collection, Acid digestion, Atomic absorption	Validation Date:	8/29/75

1. Principle of the Method

1.1 Samples are collected on filters and the sample-containing filters are wet-ashed using nitric acid and perchloric acid to destroy the organic filter matrix; zirconium and its compounds are then solubilized in an acid solution maintained at a pH of 1.

1.2 The solutions of samples and standards are aspirated into the nitrous oxide-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for zirconium is used to provide a characteristic zirconium line at 360.1 nm.

1.3 The absorption at the 360.1 nm line is proportional to the zirconium concentration in the aspirated sample.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.14-9.02 mg/cu m at an atmospheric temperature and pressure of 21°C and 766 mm Hg, using a 720-liter sample. Under the conditions of sample size (720 liters), the working range of the method is estimated to be 1-20 mg/cu m.

2.2 The method may be extended to higher concentrations by further dilution of the sample.

3. Interferences

3.1 Some experimental data indicate that the method does not work for for zirconium sulfate. This limited data may indicate that the method will not work for other zirconium compounds in the presence of sulfates. Other substances, including ammonium compounds and phosphates, are also known to interfere with the method both in the dissolution and the measurement step.

3.2 The addition of ammonium fluoride is recommended to increase sensitivity; the ammonium fluoride acts as a signal enhancer presumably by the formation of the more easily atomized fluoride specie. (Reference 11.4)

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2.14-9.02 mg/cu m was 0.053. This value corresponds to a 0.27 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 11.3.

4.2 A collection efficiency of 1.0 was determined for the collection medium; thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method--the average recovery from the filters was 101.7%. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple; however, some zirconium compounds may not be soluble in nitric acid.

6. Apparatus

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - a calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Manometer

6.1.4 Thermometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must have a nitrous oxide burner head.

6.3.1 Zirconium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used. Heating tape, with temperature controlled by a rheostat, should be wound around the 2nd stage of the nitrous oxide tank regulator and connecting hose to prevent line freeze-up during operation.

6.4 Glassware, borosilicate

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25-ml volumetric flasks

6.5 Adjustable thermostatically-controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Hot distilled water, heat to boiling

7.3 Concentrated nitric acid

7.4 Nitric acid, 1.0 N

7.5 Ammonium fluoride (NH_4F), 1.25 M. Dissolve 23.15 g of ammonium fluoride in 500 ml of water.

7.6 Commercially prepared aqueous standard zirconium stock solutions, 1000 ug/ml

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect the analyte aerosol a personal sampling pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the

filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.2 Blank. With each batch of samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every 10 samples.

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet-ashing and digestion. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process once more using 2 ml of concentrated nitric acid. Cool beaker and contents and add 3 ml of HNO_3-$HClO_4$ mixture and continue evaporating to fumes to effect complete digestion of filter. Do not allow to evaporate to dryness at any point.

8.3.3 Cool solution and add 10 ml of distilled (or deionized) water to each one.

8.3.4 Quantitatively transfer the clear solution into a 25-ml volumetric flask.

8.3.5 Rinse Phillips beaker at least twice with 5-ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.6 Add 2.0 ml of 1.25 M ammonium fluoride and dilute to 25 ml with distilled water.

8.3.7 Aspirate the solutions into a nitrous oxide-acetylene flame and record the absorbance at 360 nm. The absorbance is proportional to the sample concentration. It is recommended that the samples be frequently alternated with standards which give absorbances close to that of the sample in order to minimize the observed variations in flame characteristics and responses of the nitrous oxide-acetylene flame due to the gradual accumulation of carbon deposits

around the burner slot. These carbon deposits should be scraped off regularly.

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

8.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 720-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then ashed and analyzed as described in Section 8.3. The recovery values obtained were 101.7% and as such no correction factor has been used in the determination of the "true" values.

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

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

9. Calibration and Standards

9.1 From the 1000 µg/ml standard stock solution, prepare at least six working standards to cover the concentration range from 1000-8000 µg/25 ml. It is convenient to express the concentration in µg/25 ml because all samples are diluted to this total volume. All standard solutions are made in 0.1 N nitric acid and contain 2.0 ml of 1.25 M ammonium fluoride. The standard solutions should be prepared fresh daily.

9.2 Proceed as in Section 8.3.7 to 8.3.8.

9.3 The appropriate calibration standards are alternately analyzed with the samples to determine the appropriate calibration or response factor. This practice will minimize the effect of observed fluctuations or variations in absorbance readings during any given day.

10. Calculations

10.1 Determine the weight, in µg, corresponding to the absorbance of the sample by using the appropriate calibration or response factor determined from the response of the calibration standards. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25° C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter - mg per cu m).

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

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

11.4 Bond, A.M., Use of Ammonium Fluoride in Determination of Zirconium and Other Elements by Atomic Absorption Spectrometry in the Nitrous Oxide-Acetylene Flame, Anal. Chem. 42 (No. 8) pp. 932-935, July 1970.

Copper, Dusts and Mists

Analyte:	**Copper**	**Method No.:**	**S186**
Matrix:	**Air**	**Range:**	**0.468-1.830 mg/cu m**
OSHA Standard:	**1 mg/cu m**	**Precision ($\overline{CV}_T$):**	**0.051**
Procedure:	**Filter collection Acid digestion Atomic absorption**	**Validation Date:**	**8/29/75**

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix; copper and its compounds are then solubilized in a hydrochloric acid solution maintained at a pH of 1.

1.2 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for copper is used to provide a characteristic copper line at 324.7 nm. The absorbance is proportional to the copper concentration within a limited concentration range.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.468 to 1.830 mg/cu m at an atmospheric temperature and pressure of 25°C and 768 mm Hg, using a 90-liter sample. Under the conditions of sample size (90 liters), the working range of the method is estimated to be 0.1-3 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

There are no known interferences for the copper AA assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.468-1.830 mg/cu m was 0.051. This value corresponds to a 0.05 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 11.3.

4.2 A collection efficiency of 99.6% was determined for the collection medium at the 2X level; thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method—the average recovery from the filters was 101.0%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The analysis is both simple and specific. However, some care must be exercised to avoid contamination in water and reagents since copper is so widely distributed.

6. Apparatus

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Copper hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two stage, for each compressed gas tank used

6.4 Glassware, borosilicate:

6.4.1 125 ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25 ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water; avoid using distilled water from old tin still or those with possible copper lines.

7.2 Concentrated nitric acid

7.3 Hydrochloric acid, 6N

7.4 Aqueous standard stock solutions containing 1000 µg/ml of copper (commercially available)

7.5 Copper working standard solution, 20 µg/ml. Prepare by appropriate dilution of above solution. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect copper, dusts and mists a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5

liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers. Transfer filter to a 125 ml Phillips beaker.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process two more times using 2 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to dryness.

8.3.3 Copper dissolution. To ensure complete dissolution of copper compounds, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). This is done by adding 2 ml of 6N aqueous HCl and evaporating to about 0.5 ml; this HCl addition and evaporation step is done three times. Do not allow the solution to evaporate to dryness at any point.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 25 ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 5 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.7 Dilute all samples to 25 ml with distilled water.

8.3.8 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 324.7 nm. The absorbance

is proportional to the analyte concentration in the sample and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample could be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.6 than is necessary to effect a quantitative transfer.

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

8.3.9 Appropriate filter blanks must be analyzed by the same procedure for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm$ 5%.

For this validation study, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level was used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then extracted and analyzed as described in Section 8.4. The average recovery value obtained was found to be 101%.

The percent recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}} \times 100$$

9. Calibration and Standards

9.1 From the 20 µg/ml working standard solution, prepare at least 6 working standards to cover the range from 10 to 200 µg/25 ml. Absorbance may be a nonlinear function of copper concentration above 125 µg/25 ml (Reference 11.1) so the concentration range above 125 µg/25 ml must be adequately covered with standards. All standard solutions are made 0.2N in HCl and are stored in polyethylene bottles. Since the low concentration standards may deteriorate, the standard solutions should be made fresh each day.

9.2 Proceed as in Section 8.3.7 to 8.3.9.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled(Liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

Tellurium Hexafluoride

Analyte:	**Tellurium Hexafluoride**	**Method No.:**	**S187**
Matrix:	**Air**	**Range:**	**0.094-0.37 mg/cu m**
OSHA Standard:	0.02 ppm (0.2 mg/cu m)	Precision ($\overline{CV}_T$):	0.054
Procedure:	Adsorption on charcoal, desorption with 0.01 N sodium hydroxide, atomic absorption	Validation Date:	8/29/75

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the tellurium hexafluoride vapors present; a filter is placed before the charcoal tube to trap the particulate tellurium compounds.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 0.01 N sodium hydroxide.

   1.3 The desorbed sample is analyzed by atomic absorption spectroscopy using an air-acetylene flame and a tellurium electrodeless discharge lamp.

   1.4 The area of the resulting absorption peak at 214.3 nm is determined and compared with areas of absorption peaks obtained from injection of standards.

   1.5 In order to minimize errors due to variations in flame response, the samples must be carefully interspersed between calibration standards which give about the same response as the samples.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.094-0.373 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 390-liter sample. Under the conditions of sample size (390 liters), the probable useful range of this method is 0.04-0.6 mg/cu m. This method is capable of measuring smaller amounts if the desorption efficiency is adequate and by using scale expansion to increase instrumental response.

   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 analyte and other substances in the

air. The first section of the charcoal tube was found to hold at least 0.29 mg of analyte when a test atmosphere containing 0.63 mg/cu m of analyte in air was sampled at 1.1 liters per minute for 420 minues; i.e., at that time, the concentration of analyte 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. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, tellurium hexafluoride vapors may not be trapped efficiently.

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 Other tellurium compounds which exist as vapors will interfere with the analysis. It is expected that interference from particulate tellurium compounds may be eliminated by putting a filter cassette before the charcoal tube.

3.4 Zinc, which has a absorption line at 213.9 nm, could be a potential interfering element.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.094-0.373 mg/cu m was 0.054. This value corresponds to a 0.011 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and exrerimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 100% was determined for the collection medium; thus no bias was introduced in the sample collection step. Likewise, any bias due to analytical method recovery has been accounted for by the use of the desorption efficiency factor. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal; other than zinc, there are no known spectral line interferences for the tellurium assay. The tubes are analyzed by means of an instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When 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 personal sampling pump calibrated with a representative filter and charcoal tube in line and whose flow can be determined within +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 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tellurium electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: purified acetylene.

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used.

6.4 Volumetric flasks: 10-ml and other convenient sizes for making standards.

6.5 Pipets: Assorted sizes for making standards.

6.6 Assorted glassware.

7. Reagents

All chemicals must be ACS reagent grade or better.

7.1 Tellurium hexafluoride, gas for determining desorption efficiency.

7.2 Sodium hydroxide, 0.01 N.

7.3 Distilled water.

7.4 Tellurium standards

7.4.1 Tellurium standard stock solution, 1000 ppm. Stock solutions may be purchased from reliable suppliers.

7.4.2 Dilute tellurium stock solution (20 µg/ml). Dilute 2.0 ml of the 1000 ppm standard to 100 ml with 0.01 N sodium hydroxide. Prepare fresh daily.

7.4.3 Working standards. Prepare by diluting 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the dilute tellurium stock solution (Section 7.4.2) to 10 ml with 0.01 N sodium hydroxide. These solutions contain 10, 20, 40, 60, 80 and 100 µg/10 ml as tellurium. Multiply by 1.893 to obtain tellurium hexafluoride equivalent.

8. Procedure

8.1 Cleaning of Equipment. All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is cleaned with hot, concentrated nitric acid and thoroughly rinsed with tap water followed by distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter and 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 Connect a filter cassette holder to the front section of the charcoal tube to separate particulate tellurium compounds.

8.3.3 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

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

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

8.3.6 A sample size of 400 liters is recommended. Sample at a rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.8 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.9 One tube for every 10 samples submitted 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.

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

8.4 Analysis of Samples

8.4.1 Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file 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 a second 10-ml stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of samples. Prior to analysis, 10.0 ml of sodium hydroxide is pipetted into each sample container. Desorption should be done for 60 minutes. Tests indicate that this desorption period is adequate provided the samples are occasionally agitated by manual shaking during that period.

8.4.3 Spectrometric measurements. Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 214.3 nm. The sample concentration is proportional to the measured absorbance. Use scale expansion when necessary for low sample concentrations. Follow instrument manufacturer's recommendations for specific operating parameters.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. Thedesorption 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. A standard charcoal tube from the same batch as that used for the samples should be used. Break both ends of the tube and using a gas-tight syringe slowly add known aliquots of tellurium hexafluoride gas to the front 100 mg section of the tube. Remove the 50-mg backup section immediately after spiking and analyze this backup section to test for completeness of addition to the front section. There should be no tellurium hexafluoride in the backup section. The amount of analyte to be added is equivalent to that present in a 400-liter sample at 0.5, 1 and 2X OSHA standard level. A gas mixture of tellurium hexafluoride in air at 1:5 dilution (20%) can be used by adding 20, 40 and 80 µl aliquots to the charcoal tube.

The desorption efficiency should be determined at least in duplicate for each of these three test levels. The tubes are 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.

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

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

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 10.5 to correct for adsorption losses.

9. Calibration and Standards

9.1 Prepare a series of working standards containing 10-100 µg of tellurium in 10 ml of 0.01 N sodium hydroxide. These standards should be prepared fresh each day. Refer to Section 7.4.

9.2 To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance readings during any given day.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance of the sample by using the appropriate response factor determined from the response of the calibration standard.

10.2 Convert micrograms tellurium to micrograms tellurium hexafluoride using molecular weight ratio, 241.59/127.6 = 1.893.

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

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

where:

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

10.4 Add the amount present in the front and backup sections of the sample tube to determine the total weight in the sample.

10.5 Divide the total weight in μg found by the desorption efficiency as discussed in Section 8.5.

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

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.5)}}{\text{Air Volume Sampled (Liters)}}$$

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

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

where:

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

11. References

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

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

Rhodium, Metal Fume and Dust

Analyte:	Rhodium	Method No.:	S188
Matrix:	Air	Range:	0.057-0.21 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.079
Procedure:	Filter collection, Acid digestion, Atomic absorption,	Validation Date:	8/29/75

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix; rhodium and its compounds are then solubilized in a hydrochloric acid solution maintained at a pH of 1; potassium bisulfate is added to eliminate interferences by other common cations.

1.2 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for rhodium is used to provide a characteristic rhodium line at 343.5 nm. The absorbance is proportional to the rhodium concentration within a limited concentration range.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.057-0.21 mg/cu m at an atmospheric temperature and pressure of 24°C and 756 mm Hg, using a 720-liter sample. Under the conditions of sample size (720 liters), the linear working range of the method is estimated to be 0.005-0.21 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

Addition of 3% potassium bisulfate eliminates the interferences of other common cations, and also anions like nitrates and phosphates in the rhodium assay using an oxidizing air-acetylene flame (Reference 11.4).

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.057-0.21 mg/cu m was 0.079. This value corresponds to a 0.0079 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 11.3.

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 may be some bias in the analytical method--the average recovery from the filters was 94.7%; the data may be adjusted by this correction factor to eliminate any bias. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manomemter

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Rhodium hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two stage, for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25-ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Hydrochloric acid, 6N

7.4 Potassium bisulfate, $KHSO_4$. Prepare a 30% (w/v) solution in water.

7.5 Aqueous standard rhodium stock solution, 1000 µg/ml. (Commercially available)

7.6 Rhodium working standard solution, 20 µg/ml. Prepare by appropriate dilution of above solution. Prepare fresh daily.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect rhodium, metal fume and dust, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the

filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125 ml Phillips beaker.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process two more times using 2 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to dryness.

8.3.3 Rhodium dissolution. To ensure complete dissolution of rhodium compounds, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). This is done by adding 2 ml of 6 N aqueous HCl and evaporating to about 0.5 ml; this HCl addition and evaporation is done 3 times. Do not allow the solution to evaporate to dryness at any point.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 5-ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.7 Add 2.5 ml of the 30% potassium bisulfate solution and dilute to 25 ml with distilled water.

8.3.8 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 343.5 nm. The absorbance

is proportional to the analyte concentration in the sample and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample could be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.6 than is necessary to effect a quantitative transfer.

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

8.3.9 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the concentration expected in the sample, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 720-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value obtained was found to be 95%.

The percent recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}} \times 100$$

9. Calibration and Standards

9.1 From the 20 µg/ml working standard solution, prepare at least 6 working standards to cover the range from 10 to 160 µg/25 ml.

Absorbance may be a nonlinear function of rhodium concentration above 160 µg/25 ml (Reference 11.1) so the concentration range above 160 µg/25 ml must be adequately covered with standards. All standard solutions are made 0.2N in HCl and are stored in polyethylene bottles. Since the low concentration standards may deteriorate, the standard solutions should be made fresh each day.

9.2 Proceed as in Section 8.3.7 to 8.3.9.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

11.4 Kallmann, S. and Hobart, E.W., "Vital Parameters in the Determination of Rhodium by Atomic Absorption", Anal. Chim. Acta 51, 120-124 (1970).

Rhodium, Soluble Salts

Analyte:	Rhodium	Method No.:	S189
Matrix:	Air	Range:	0.0004-0.0018 mg/cu m
OSHA Standard:	0.001 mg/cu m	Precision ($\overline{CV}_T$):	0.069
Procedure:	Filter collection, Acid digestion, AA/high temperature graphite atomizer	Validation Date:	8/29/75

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid and perchloric acid to destroy the organic matrix; rhodium and its compounds are then solubilized in an acid solution maintained at a pH of 1.

1.2 The solutions of samples and standards are analyzed by flameless atomic absorption spectroscopy in a heated graphite atomizer.

1.3 The area of the resulting absorption peak at 369.5 nm is determined and compared with areas of absorption peaks obtained from injection of standards.

1.4 The samples must be carefully interspersed between calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.0004-0.0018 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 370-liter sample. Under the conditions of sample size (370 liters), the linear working range of the method is estimated to be 0.0002-0.003 mg/cu m when the total sample collected is diluted to 25 ml and a 50-microliter aliquot is analyzed.

2.2 The lower limit of detection for a 50-microliter sample aliquot is 0.003 micrograms per ml.

3. Interferences

There are no known interferences to the rhodium assay using the high temperature graphite accessory.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.0004-0.0018 mg/cu m was 0.069. This value corresponds to a 0.000069 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 11.3.

4.2 A collection efficiency of 99.6 $\pm$ 0.9% was determined for the collection medium; thus, no bias was introduced in the sample collection step. There may be some bias in the analytical method--the average recovery from the filters was 105%; the data may be adjusted by this correction factor to eliminate any bias. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is tedious and requires a high degree of technical skill.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer having a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and deuterium background corrector accessory. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 369.5 nm wavelength.

6.4 The rhodium radiation source may be either an electrodeless discharge lamp or a hollow cathode lamp. The former is recommended because it is a brighter source.

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

6.6 Eppendorf automatic pipettor with disposable plastic pipets for accurately injecting 50-microliter sample aliquots into the graphite furnace tube.

6.7 Glassware, borosilicate:

6.7.1 125-ml Phillips beakers with watchglass covers

6.7.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.7.3 25-ml volumetric flasks

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

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Perchloric acid

7.4 Nitric Acid - Perchloric Acid Mixture (2 parts HNO_3 + 1 part $HClO_4$)

7.5 Rhodium Standards

7.5.1 Rhodium standard stock solution, 1000 µg/ml, (Commercially available from reliable suppliers such as Fisher Scientific).

7.5.2 Dilute rhodium stock solution, 1 µg/ml. Prepare by appropriate (preferably sequential) dilution of above solution. Prepare fresh daily in 0.01M nitric acid.

7.5.3 Working standards. Prepare by diluting 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, and 1.2 ml of the dilute rhodium stock solution (Section 7.5.2) to 25 ml with 0.01 M nitric acid. These solutions contain rhodium in the concentration range of 0.004 to 0.048 µg/ml. Prepare solutions fresh daily.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect rhodium soluble salts, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet ashing and digestion. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process once more using 2 ml of concentrated nitric acid. Cool beaker and contents and add 3 ml of HNO_3-$HClO_4$ mixture and continue evaporating to fumes to effect complete digestion of filter. Do not allow to evaporate to dryness at any point.

8.3.3 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.4 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.

8.3.5 Rinse each beaker at least twice with 5-ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask and dilute to 25 ml.

8.3.6 Spectrophotometric measurements.

1. The instrumental parameters for source power, background corrector, and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying and atomization should be established in accordance with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of rhodium during these steps.

2. Inject a 50-microliter aliquot of the sample solution into the graphite tube using an automatic pipettor with disposable plastic tips.

3. A minimum of duplicate analyses per sample should be done.

4. To obtain reliable results, samples must be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, ...etc.

NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak areas, it must be rejected and replaced because results so obtained are not reliable.

8.3.7 Measurement of Area. The area of the absorption peak is measured by some suitable form of area measurement such as a planimeter or an electronic integrator. Note that peak height measurements will give neither precise nor reliable results.

8.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the concentration expected in the sample, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 370-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value obtained was found to be 105%.

The percent recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}} \times 100$$

9. Calibration and Standards

9.1 Prepare a series of working standards containing 0.1 to 1.2 micrograms of rhodium in 25 ml of 0.01 M nitric acid. These standards should be prepared fresh each time. Refer to Section 7.5.3.

9.2 The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor for the sample.

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

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

where:

μg sample = μg found in sample filter
μg blank = μg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample

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

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

Selenium Compounds (as Se)

Analyte:	Selenium	Method No.:	S190
Matrix:	Air	Range:	0.10-0.50 mg/cu m
OSHA Standard:	0.2 mg/cu m	Precision ($\overline{CV}_T$):	0.090
Procedure:	Filter collection Acid extraction Atomic absorption	Validation Date:	8/29/75

1. Principle of the Method

1.1 Sample-containing filters are treated with 0.1 N nitric acid to extract the selenium compound from the filter. The applicability of the method is limited to selenium compounds which are soluble in the acid media. Bulk samples should be tested to verify solubility.

1.2 The solutions of samples and standards are aspirated into the argon hydrogen flame of an atomic absorption (AA) spectrophotometer. An electrodeless discharge lamp for selenium is used to provide a characteristic selenium line at 196.0 nm. The absorbance is proportional to the selenium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.10-0.50 mg/cu m at an atmospheric temperature and pressure of 19°C and 762 mm Hg, using a 360-liter sample. Under the conditions of sample size (360 liters), the linear working range of the method is estimated to be 0.05-0.60 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

There is no known spectral line interference due to other elements. The selenium assay requires an instrument with a background corrector in order to compensate for potential interferences such as those caused by the presence of salts. Since the main absorption line is below 200 nm, the flame characteristics will strongly influence the measurable signal due to oxygen absorption in the atomization process. The use of carbonaceous fuels like air-acetylene should be avoided.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.10-0.50 mg/cu m was 0.090. This value corresponds to a 0.018 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 11.3.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. Any bias due to analytical recovery which averages 92% over the concentration range of 0.5 to 2X OSHA standard for a 360-liter sample has been accounted for by correcting the "found" values using this recovery factor. 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 method is simple.

5.2 The method is limited only to selenium compounds which are soluble in acid media.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for an argon/hydrogen-air flame and a background corrector.

6.3.1 Selenium electrodeless discharge lamp

6.3.2 Air

6.3.3 Fuel: Argon-hydrogen

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards.

6.4.3 25-ml volumetric flasks

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Nitric acid, 0.1 N

7.3 Aqueous standard selenium stock solution, 1000 µg/ml. Commercially available.

7.4 Selenium working standard solution, 100 µg/ml. Prepare fresh daily by appropriate dilution of the stock standard solution with 0.1 N nitric acid.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect particulate selenium compounds, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder

is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassette should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker.

8.3.2 Extraction of samples. Treat the filter in the beaker with 10 ml of 0.1 N nitric acid and allow to stand for at least 20 minutes occassionally swirling the contents of the flask to aid the sample extraction. Do not use an ultrasonic agitator because the filter will disintegrate and will require an additional configuration step to allow the filter fibers to settle. After 20 minutes, quantitatively transfer the supernatant liquid into a 25-ml volumetric flask. Repeat the filter extraction with 5 ml of 0.1 N nitric acid two more times and quantitatively transfer all rinsings into the 25-ml volumetric flask. Dilute to volume with 0.1 N nitric acid.

8.3.3 Aspirate the solutions into an argon/hydrogen-air flame and record the absorbance at 196.0 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response.

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

8.3.4 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. Use known amounts of the "bulk sample" for this determination. A known amount of the analyte, present in the "bulk sample", preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within ± 5%.

For this validation study, an amount of the analyte equivalent to that present in a 360-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly by adding aliquots of an aqueous solution of potassium selenite. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 92%.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 From the selenium working standard solution, prepare at least six standard solutions to cover the selenium concentration range from 10-200 µg/25 ml. Prepare these standard solutions fresh daily using 0.1 N nitric acid for all dilutions.

9.2 Proceed as in Section 8.3.3.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V^s = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

Platinum, Soluble Salts as Pt

Analyte:	Platinum	Method No.:	S191
Matrix:	Air	Range:	0.00079-0.0031 mg/cu m
OSHA Standard:	0.002 mg/cu m	Precision ($\overline{CV}_T$):	0.062
Procedure:	Filter collection, Acid digestion, AA/high temperature graphite atomizer	Validation Date:	8/29/75

1. Principle of the Method

   1.1 Sample-containing filters are wet-ashed using nitric acid and perchloric acid to destroy the organic matrix; platinum and its compounds are then solubilized in an acid solution.

   1.2 The solutions of samples and standards are analyzed by flameless atomic absorption spectroscopy in a heated graphite atomizer.

   1.3 The area of the resulting absorption peak at 265.9 nm is determined and compared with areas of absorption peaks obtained from injection of standards.

   1.4 The samples must be carefully interspersed between calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.00079-0.0031 mg/cu m at an atmospheric temperature and pressure of 24°C and 767 mm Hg, using a 720-liter sample. Under the conditions of sample size (720 liters), the linear working range of the method is estimated to be 0.0004-0.0060 mg/cu m when the total sample collected is diluted to 25 ml and a 50-microliter aliquot is analyzed.

   2.2 The lower limit of detection for a 50-microliter sample aliquot is 0.010 micrograms per ml.

3. Interferences

   There are no known interferences to the platinum assay using the high-temperature graphite accessory.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.00079-0.0031 mg/cu m was 0.062. This value corresponds to a 0.00012 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 11.3.

4.2 A collection efficiency of 99.7 $\pm$ 0.6% was determined for the collection medium; thus, no bias was introduced in the sample collection step. Likewise, there is no bias in the analytical method--the average recovery from the filters was 97%. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is tedious and requires a high degree of technical skill; however, it is the only one sensitive enough to analyze personal air samples.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm, 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer having a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and deuterium background corrector accessory. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 265.9 nm wavelength.

6.4 The platinum radiation source may be either an electrodeless discharge lamp or a hollow cathode lamp. The former is recommended because it is a brighter source.

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

6.6 Eppendorf automatic pipettor with disposable plastic pipets for accurately injecting 50-microliter sample aliquots into the graphite furnace tube.

6.7 Glassware, borosilicate:

6.7.1 125-ml Phillips beakers with watchglass covers

6.7.2 Pipets, delivery or graduated, 1, 5, 10-ml

6.7.3 25-ml volumetric flasks

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

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Perchloric acid

7.4 Nitric Acid - Perchloric Acid Mixture (2 parts HNO_3 + 1 part $HClO_4$)

7.5 Platinum Standards

7.5.1 Platinum standard stock solution, 1000 µg/ml, (commercially available from reliable suppliers such as Fisher Scientific).

7.5.2 Dilute platinum stock solution, 1 µg/ml. Prepare by appropriate (preferably sequential) dilution of above solution. Prepare fresh daily in 0.01 M nitric acid.

7.5.3 Working standards. Prepare by diluting 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of the dilute platinum stock solution (Section 7.5.2) to 25 ml with 0.01 M nitric acid. These solutions contain platinum in the concentration range of 0.020 to 0.120 µg/ml. Prepare solutions fresh daily.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect platinum soluble salts, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet-ashing and digestion. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process once more using 2 ml of concentrated nitric acid. Cool beaker and contents and add 3 ml of HNO_3-$HClO_4$ mixture and continue evaporating to fumes to effect complete digestion of filter. Do not allow to evaporate to dryness at any point.

8.3.3 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.4 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.

8.3.5 Rinse each beaker at least twice with 5-ml portions of distilled water, and quantitatively transfer each rinsing

to the solution in the volumetric flask and dilute to 25 ml.

8.3.6 Spectrophotometric measurements.

1. The instrumental parameters for source power, background corrector, and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying and atomization should be established in accordance with the manufacturer's recommendations. Note, however, that in order to avoid premature loss of platinum, the following drying and charring conditions should be observed:

Sample Cycle	Time in Seconds	Temperature, °C
Sample drying	40	150
Sample charring	20	500
Sample atomization	10	2700

2. Inject a 50-microliter aliquot of the sample solution into the graphite tube using an automatic pipettor with disposable plastic tips

3. A minimum of duplicate analyses per sample should be done.

4. To obtain reliable results, samples must be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, ...etc.

   NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak areas, it must be rejected and replaced because results so obtained are not reliable.

8.3.7 Measurement of Area. The area of the absorption peak is measured by some suitable form of area measurement, such as a planimeter or an electronic integrator. Note that the peak height measurements will not give precise nor reliable results.

8.3.8 Appropriat filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the concentration expected in the sample, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within ± 5%.

For this validation study, an amount of the analyte equivalent to that present in a 720-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value obtained was found to be 97%.

The recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 Prepare a series of working standards containing 0.5 to 3.0 micrograms of platinum in 25 ml of 0.01 M nitric acid. These standards should be prepared fresh each time. Refer to Section 7.5.3.

9.2 The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor for the sample.

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

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

where:

μg sample = μg found in sample filter
μg blank = μg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample.

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

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

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation, Norwalk, Conn., 1971

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

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

Molybdenum, Soluble Compounds

Analyte:	Molybdenum	Method No.:	S193
Matrix:	Air	Range:	1.96-9.75 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.089
Procedure:	Filter collection, Hot water leaching, Atomic absorption	Validation Date:	8/29/75

1. Principle of the Method

   1.1 Samples are collected on filters and leached off the filter with hot water.

   1.2 The solutions of samples and standards are aspirated into the nitrous oxide-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for molybdenum is used to provide a characteristic molybdenum line at 313.3 nm.

   1.3 The absorption at the 313.3 nm line is proportional to the molybdenum concentration in the aspirated sample within a limited concentration range.

2. Range and Sensitivity

   2.1 This method was validated over the range of 1.96-9.75 mg/cu m at an atmospheric temperature and pressure of 26°C and 760 mm Hg, using a 90-liter sample. Under the conditions of sample size (90 liters), the linear working range of the method is estimated to be 0.5-15 mg/cu m.

   2.2 The method may be extended to higher concentrations by further dilution of the sample and also to lower concentrations by collecting a larger sample volume.

3. Interferences

   The variable enhancement which would result from the presence of small amounts of aluminum and traces of acidity are alleviated by adding to the sample solution the equivalents of aluminum and nitric acid to maintain an aluminum concentration of 400 µg/ml and an acid strength of 0.1 N.

4. Precision and Accuracy

   4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.96-9.75 mg/cu m was 0.089. This value corresponds to a 0.45 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 11.3.

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. Likewise, there was no bias in the analytical method--the average recovery from the filters was 100.5%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple.

6. Apparatus

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of metal content has the following components;

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Manometer

6.1.4 Thermometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must be equipped with a nitrous oxide-acetylene burner head.

6.3.1 Molybdenum hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two stage, for each compressed gas tank used; heating tape with temperature controlled by a rheostat is wound around the second stage of the nitrous oxide regulator and the connecting hose to prevent freeze-up of the line.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25-ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Hot distilled water, heat to boiling

7.3 Concentrated nitric acid

7.4 Nitric acid, 1.0 N

7.5 Commercially prepared aqueous aluminum solution, 10,000 µg/ml

7.6 Commercially prepared aqueous standard molybdenum stock solutions, 1000 µg/ml

7.7 Molybdenum working standard solution, 100 µg/ml. Prepare by appropriate dilution of above stock solution. Prepare fresh daily.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect the analyte aerosol a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1) The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of

the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the filter from the holder and cellulose backup pad with the aid of filter tweezers.

8.3.2 Transfer the filter to a clean 125 ml Phillips beaker.

8.3.3 Add 10 ml of hot (boiling) distilled water and allow to stand 10 minutes with occasional swirling.

8.3.4 Quantitatively transfer the water extract into a 25-ml volumetric flask.

8.3.5 Rinse Phillips beaker and filter at least twice with 5 ml portions of hot distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.6 Add 2.5 ml of 1 N nitric acid and 1 ml of aluminum solution containing 10,000 µg/ml.

8.3.7 Allow to cool and dilute to 25 ml with distilled water.

8.3.8 Aspirate the solutions into a nitrous oxide-acetylene flame and record the absorbance at 313.3 nm. The absorbance is proportional to the molybdenum concentration in the sample. It is recommended that the samples be frequently alternated with standards which give absorbances close to that of the sample in order to minimize the observed variations in flame characteristics and responses of the nitrous oxide-acetylene flame due to the gradual accumulation of carbon deposits around the burner slot. These carbon deposits should be scraped off regularly.

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

8.3.9 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then extracted and analyzed as described in Section 8.3. The recovery values obtained were 100% and as such no correction factor has been used in the determination of the "true" values.

The percent recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}} \times 100$$

9. Calibration and Standards

9.1 From the 100 µg/ml working standard solution, prepare at least six working standards to cover the concentration range from 50-1000 µg/25 ml. It is convenient to express the concentration in µg/25 ml because all samples are diluted to this total volume. All standard solutions are made in 0.1 N nitric acid; the standard solutions should be prepared fresh daily.

9.2 Proceed as in Section 8.3.6 to 8.3.9.

9.3 The appropriate calibration standards are alternately analyzed with the samples to determine the appropriate calibration or response factor. This practice will minimize the effect of observed fluctuations or variations in absorbance readings during any given day.

10. Calculations

10.1 Determine the weight, in µg, corresponding to the absorbance of the sample by using the appropriate calibration or response factor determined from the response of the standards. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn. 1971.

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

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

Barium, Soluble Compounds

Analyte:	Barium	Method No.:	S198
Matrix:	Air	Range:	0.281-1.084 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	Filter collection, hot water leaching, atomic absorption	Validation Date:	9/26/75

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

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are leached in hot water. The soluble portion is decanted, filtered, dried, and then dissolved in dilute hydrochloric acid containing sodium chloride.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.281-1.084 mg/cu m using a 168-liter sample at an atmospheric temperature and pressure of 24°C and 747 mm Hg. Under the conditions of sample size (168 liters), the working range of the method is estimated to be 0.15-1.3 mg/cu m.

   2.2 The sensitivity of this method using the 5-ml final solution volume is 2 µg (0.4 µg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using longer sampling times or by scale expansion to increase instrumental response.

3. Interferences

   Ionization of barium in the flame is a problem in the determination of barium by atomic absorption spectrophotometry. This can be controlled by the addition of 1000-2000 µg/ml of sodium (as sodium chloride) to the samples and standards.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.281-1.084 mg/cu m is 0.054. This value corresponds to a 0.027 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was no bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

5.2 This method measures those barium compounds as soluble if they dissolve from the collection filter in boiling water. There is a wide range of solubilities among barium compounds, and this classification may be a disadvantage in some cases.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of barium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of + 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochomator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with a nitrous oxide-acetylene burner head.

6.3.1 Barium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: acetylene

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

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water).

7.4 Sodium chloride.

7.5 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of barium.

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Add 10 ml of boiling distilled water to each beaker. Leach each sample for 10 minutes with occasional swirling.

8.4.3 Decant each solution into a second clean 125-ml Phillips beaker. Wash the original beaker and filter twice with hot distilled water and add to the second beaker.

8.4.4 Repeat the leaching process on the filter, decanting and washing all solutions into the same second beaker (i.e., repeat steps 8.4.2 and 8.4.3).

8.4.5 Remove each filter with clean ivory tipped forceps and wash each side of the filter with a stream of hot distilled water into the second beaker.

8.4.6 Rinse carefully the inside of the original beaker three times with hot distilled water and add to the second beaker. Carefully filter the solutions through a Buchner funnel to thoroughly remove any insoluble barium compounds collected.

8.4.7 Add three drops of concentrated hydrochloric acid to each of the samples, and then evaporate the solution to dryness.

8.4.8 Cool each beaker and dissolve the residues in 5 ml of dilute hydrochloric acid (5 ml of concentrated hydrochloric acid diluted to 100 ml with distilled water) containing 1100 ppm of sodium added as sodium chloride (0.28 g of sodium chloride/ 100 ml of dilute hydrochloric acid).

8.4.9 After the residue is dissolved, aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 553.6 nm. The absorbance is proportional to the barium concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase the instrument response.

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

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

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 40 to 200 µg/5 ml from the 1000 µg/ml stock barium standard solution. Make all standard solutions in dilute hydrochloric acid containing 1100 ppm of sodium added as sodium chloride and prepare fresh daily.

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

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/5 ml.

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

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

where:

µg sample = µg found in sample filter

µg blank = µg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Yttrium

Analyte:	Yttrium	Method No.:	S200
Matrix:	Air	Range:	0.529-2.211 mg/cu m
OSHA Standard:	1 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

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

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the yttrium is then dissolved in hydrochloric acid.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.529-2.211 mg/cu m using a 500-liter sample at an atmospheric temperature and pressure of 24.5°C and 745 mm Hg. Under the conditions of sample size (500 liters), the working range of the method is estimated to be 0.15-5 mg/cu m.

   2.2 The sensitivity of this method using the 5-ml final solution volume is 10 µg (2 µg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   The presence of aluminum, potassium, and phosphoric acid in the flame are known to depress the absorbance by yttrium. Also yttrium is partially ionized in the nitrous oxide-acetylene flame. These effects can be overcome by the addition of 1000 ppm sodium (as NaCl) to samples and standards.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.529-2.211 mg/cu m is 0.054. This value corresponds to a 0.054 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, 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 quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of yttrium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

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

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with a nitrous oxide-acetylene burner head.

6.3.1 Yttrium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: acetylene

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

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Yttrium metal, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 0.6 M hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water). To this solution add 250 mg of NaCl. The HCl solution will contain 1000 ppm of sodium.

7.5 6 M hydrochloric acid.

7.6 Perchloric acid, 60% solution.

7.7 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of yttrium.

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A minimum sample size of 500 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 **Wet Ashing:** Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of the beaker, and allow the solution to evaporate to dryness.

8.4.3 Yttrium nitrate and perchlorate are soluble in hydrochloric acid and no special precaution is needed to solubilize the yttrium.

8.4.4 Cool each beaker and dissolve residues in 5 ml 0.6 M hydrochloric acid which contains 1000 ppm sodium. The addition of the hydrochloric acid must be quantitative.

8.4.5 When the residue is completely dissolved, aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 410.2 nm. The absorbance is proportional to the yttrium concentration and can be determined from the appropriate calibration curve.

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

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

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of three levels (0.5X, 1X, and 2X the OSHA standard). Appropriate amounts of yttrium metal are dissolved in 25 ml of 6 M HCl and 2-3 drops of concentrated nitric acid and diluted to 100 ml with distilled water to represent each of the three levels. Three sets of six filters are spiked with appropriate volumes of each standard solution for each of the three levels. This corresponds to the amount of yttrium collected in a 500-liter sample at the 0.5X, 1X, and 2X levels, respectively. Allow the

filters to dry and place each filter in a cassette filter holder, and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

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

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

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 150 to 1500 µg/5 ml from the 1000 µg/ml stock yttrium standard solution. Make all standard solutions in 0.6M hydrochloric acid containing 1000 ppm sodium. Prepare fresh working standards daily.

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

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/5 ml.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

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

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

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Tellurium

Analyte:	Tellurium	Method No.:	S204
Matrix:	Air	Range:	0.0495-0.240 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision (CV_T):	0.055
Procedure:	Filter collection, Acid digestion, Atomic absorption	Validation Date:	9/26/75

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

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the tellurium is then dissolved in dilute nitric acid solution.

   1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). An electrodeless discharge lamp for tellurium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.0495-0.240 mg/cu m using a 670-liter sample at an atmospheric temperature and pressure of 22.5°C and 746 mm Hg. Under the conditions of sample size (670 liters), the working range of the method is estimated to be 0.02-0.4 mg/cu m.

   2.2 The sensitivity of this method using the 5-ml final solution volume is 2.5 micrograms (0.5 microgram/ml for 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by scale expansion to increase instrumental response.

3. Interferences

   There are no known interferences for the tellurium AAS assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.0495-0.240 mg/cu m is 0.055. This value corresponds to a 0.006 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no bias in the sampling and analytical method. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of tellurium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

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

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tellurium electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

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

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute nitric acid (10 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water).

7.4 Perchloric acid, 60% solution.

7.5 Commercially prepared aqueous standard stock solutions; 1000 micrograms Te/ml.

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 670 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of ±5%.

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

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated.

Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Caution must be taken when using perchloric acid to destroy the filter. Cover each beaker with a watchglass and heat on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate to dryness.

8.4.3 The tellurium compounds are soluble in nitric acid and no special precaution is needed to solubilize them.

8.4.4 Cool each beaker and quantitatively add 5 ml of dilute nitric acid.

8.4.5 After the samples are dissolved aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 214.3 nm. The absorbance is proportional to the tellurium concentration which can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response.

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

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

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 20-400 micrograms/5 ml from the 1000 micrograms/ml stock tellurium standard solution. All standard solutions are made in dilute nitric acid and are prepared fresh daily.

9.2 Aspirate each of the standard solutions and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram/5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in microgram, corresponding to the total absorbance, from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/5 ml.

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

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

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Calcium Oxide

Analyte:	Calcium Oxide	Method No.:	S205
Matrix:	Air	Range:	2.6-10.16 mg/cu m
OSHA Standard:	5 mg/cu m	Precision (CV_T):	0.063
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

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

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and any organic material, and the calcium oxide is then solubilized in hydrochloric acid.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 2.6-10.16 mg/cu m using an 85-liter sample at an atmospheric temperature and pressure of 23.5°C and 744.5 mm Hg. Under the conditions of sample size (85 liters), the working range of the method is estimated to be 1-20 mg/cu m.

2.2 The sensitivity of this method using the 100-ml final solution volume is 10 µg of calcium (0.1 µg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response. To maintain a linear calibration curve over the range of 10-20 mg/cu m of calcium, an alternate calcium line (239.9 nm), sample dilution, burner repositioning, or other suitable means must be employed

3. Interferences

3.1 Interferences to the calcium atomic absorption spectrophotometric assay include Si, Al and PO_4^{-3}, which are controlled by the addition of La at 1% (1 g/100 ml) to both standards and samples.

3.2 Alkali type metals such as sodium, potassium, lithium, and magnesium suppress ionization, thus enhancing the response to calcium, and cause a positive interference.

3.3 Calcium compounds other than calcium oxide will also be measured as the oxide, resulting in a high reading.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range 2.6-10.16 mg/cu m is 0.063. This value corresponds to a 0.32 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no bias in the sampling and analytical method. Thus, 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 quick, instrumental method.

5.2 This method is not specific for calcium oxide. Other calcium compounds which are collected on the filter will be measured.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of calcium oxide content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 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.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Calcium hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: acetylene

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

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25 and 100-ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Double distilled water

7.2 Concentrated nitric acid

7.3 Dilute hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water) containing 1% La (1 g La/100 ml)

7.4 Perchloric acid, 60% solution

7.5 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of calcium (1400 µg/ml calcium oxide)

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 85 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of the beaker, and allow the solution to evaporate to dryness.

8.4.3 Cool each beaker and dissolve residues in 5 ml dilute hydrochloric acid containing 1% La. Calcium and its compounds are soluble in hydrochloric acid and no special precaution is needed to solubilize the calcium compounds.

8.4.4 Quantitatively transfer the clear solutions to a 100-ml volumetric flask.

8.4.5 Rinse each beaker at least twice with 5 ml portions of dilute hydrochloric acid (containing 1% La) and quantitatively transfer each rinsing to the volumetric flask. Dilute all samples to 100 ml with dilute hydrochloric acid (containing 1% La).

8.4.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 422.7 nm. The absorbance is proportional to the calcium oxide concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the solution can be evaporated to a small volume and diluted to a volume such as 25 or 50 ml before aspiration. In such a case use no more acid solution in 8.4.5 than is necessary to effect a quantitative transfer.

Note: The lanthanum is added to prevent formation of calcium oxide molecules in the flame and to prevent interference from Si, Al, and $PO_4^{\equiv}$. Follow the instrument manfacturer's recommendations for specific AAS operating parameters.

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

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 100 to 1500 µg/100 ml calcium from the 1000 µg/ml stock calcium standard solution (140 to 2100 µg/100 ml of calcium oxide). Make all standard solutions in dilute hydrochloric acid (containing 1% La). Prepare fresh working standards each day.

9.2 Aspirate each of the standards and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/100 ml of calcium oxide. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/100 ml.

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

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

where

μg sample = µg found in sample filter

μg blank = µg found in blank filter

10.3 Calculate the µg of calcium oxide by multiplying the µg of calcium found (Section 10.2) by 1.40, which is a conversion factor to convert µg calcium to µg calcium oxide.

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Nickel, Metal and Soluble Compounds (as Ni)

Analyte:	Nickel	Method No.:	S206
Matrix:	Air	Range:	0.447-2.075 mg/cu m
OSHA Standard:	1 mg/cu m	Precision ($\overline{CV}_T$):	0.057
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

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

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the nickel (including nickel compounds) is then dissolved in nitric acid.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.447-2.075 mg/cu m using an 85-liter sample at an atmospheric temperature and pressure of 26.5°C and 745 mm Hg. Under the conditions of sample size (85 liters), the working range of the method is estimated to be 0.4-8 mg/cu m.

   2.2 The sensitivity of this method using the 25-ml final solution volume is 2.5 μg (0.1 μg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   There are no known interferences for the nickel atomic absorption spectrophotometric assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.447-2.075 mg/cu m is 0.057. This value corresponds to a 0.057 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Nickel hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: acetylene

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

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 25 and 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute nitric acid (5 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water).

7.4 Perchloric acid, 60% solution.

7.5 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of nickel.

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated.

Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse the sides of the beaker, and allow the solution to evaporate to dryness.

8.4.3 Nickel and its compounds are soluble in nitric acid and no special precaution is needed to solubilize the nickel.

8.4.4 Cool each beaker and dissolve residues in 5 ml dilute nitric acid.

8.4.5 Quantitatively transfer the clear solutions to a 25-ml volumetric flask.

8.4.6 Rinse each beaker at least twice with 5-ml portions of dilute nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 25 ml with dilute nitric acid.

8.4.7 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 232.0 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume such as 5 or 10 ml before aspiration. In such a case use no more acid solution in 8.4.6 than is necessary to effect a quantitative transfer.

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

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

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 12.5 to 250 µg/25 ml from the 1000 µg/ml stock nickel standard solution. Make all standard solutions in dilute nitric acid and prepare fresh daily.

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

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in μg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg/25 ml.

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

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

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Tributyl Phosphate

Analyte:	Tributyl Phosphate	Method No.:	S208
Matrix:	Air	Range:	2.7-12.6 mg/cu m
OSHA Standard:	5.0 mg/cu m	Precision ($\overline{CV}_T$):	0.076
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date:	11/21/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and extracted with ether.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).

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

2. Range and Sensitivity

2.1 This method was validated over the range of 2.7-12.6 mg/cu m at an atmospheric temperature and pressure of 19°C and 761 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 1.5-mg sample.

2.2 The upper limit of the range of the method is dependent on the filtration capacity 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 tributyl phosphate aerosol was found to be 100% when sampled for 66 minutes at 1.5 liters per minute from a test atmosphere containing 12.6 mg/cu m and at an atmospheric temperature and pressure of 19°C and 761 mm Hg.

3. Interferences

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

3.2 Dibutyl phosphate frequently coexists with tributyl phosphate. However dibutyl phosphate is non-volatile and does not interfere with the gas chromatographic analysis of tributyl phosphate.

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

3.4 At higher atmospheric temperatures some distribution between tributyl phosphate particulate and vapor may occur which can yield erroneous values if only the front filter is analyzed. The vapor is absorbed to a limited extent by the cellulose backup pad. Refer to Section 8 for Sample Collection and Analysis.

Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.7-12.6 mg/cu m was 0.076. This value corresponds to a standard deviation of 0.38 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 100% was determined for the collecting medium under special consideration of atmospheric temperature and pressure noted. Thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery from the filters was 100.4%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

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

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37-mm, 3-piece cassette filter holder. Front and backup filter units are needed when sampling atmospheres at temperatures above 23°C.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with the representative filter holders and filters in the line.

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 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 3% OV-101 on 100/120 mesh Supelcoport, or equivalent column capable of achieving the desired resolution.

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

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.

6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Anhydrous ether, reagent grade

7.2 Tributyl phosphate, reagent grade

7.3 Purified hydrogen

7.4 Prefiltered, compressed air

7.5 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 the representative filter cassettes 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 connect the cassette filter to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

Note: If the ambient temperature to be sampled is above 23°C, use two filter cassettes connected in series with a short piece of flexible tubing for sample collection. This arrangement is necessary because some tributyl phosphate vapor may exist at temperatures above 23°C.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassettes.

8.3.4 A sample size of 100 liters is recommended, but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

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

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

8.3.7 Separate the front and backup filter cassettes (if two cassettes were used) and seal. Collected sample cassettes should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity including front and backup filter designation, if any, and all relevant sample data.

8.3.9 **Blank: With each batch of 10 samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.**

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

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. **Open the cassette filter holder and carefully transfer the cellulose membrane filter and cellulose backup pad with the aid of Millipore filter tweezers to the jar. (Both filter and pad are analyzed.)**

2. **Pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.**

3. **Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.**

4. **The front filter/pad and backup filter/pad should be analyzed. This applies to sampling at temperatures above 23°C.**

8.4.2 GC Conditions. The typical operating condtions for the gas chromatograph are:

1. 50 ml/min (50 psig) Nitrogen carrier gas flow
2. 70 ml/min Hydrogen gas flow to detector
3. 150 ml/min air flow to detector
4. 240°C injector temperature
5. 240°C detector temperature
6. 150°C column temperature

8.4.3 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 technique.

8.4.4 Measurement of area. The total area of the 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 in Section 9.

8.5 Determination of Sample Recovery

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

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to 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. Duplicate determinations should agree within $\pm$5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) have been dosed accordingly using a solution of tributyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4.

The average recovery value obtained was 100% and as such no correction factor has been used in the determination of the "true" values.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and, therefore, it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg per 10.0 ml ether, and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Add the amount found in the front filter/pad and backup filter/pad to determine total weight in the sample. This applies to samples collected at temperatures above 23°C.

10.4 Divide the total weight by the recovery to obtain the corrected µg/sample.

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

10.5 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
p = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{\text{Air Volume Sampled (Liter)}}$$

11. Reference

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

Triorthocresyl Phosphate

Analyte:	Triorthocresyl Phosphate	Method No.:	S209
Matrix:	Air	Range:	0.029-0.170 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.086
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date:	11/21/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and extracted with ether.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).

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

2. Range and Sensitivity

2.1 This method was validated over the range of 0.029-0.170 mg/cu m at an atmospheric temperature and pressure of 19°C and 761 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.02-0.3 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 30-microgram sample.

2.2 The upper limit of the range of the method is dependent on the filtration capacity 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 triorthocresyl phosphate aerosol was found to be 99% when sampled for 66 minutes at 1.5 liters per minute (100 liters) from a test atmosphere containing 0.17 mg/cu m. Similarly, the collection efficiency was found to be 99% for a 150-liter sample at 0.19 mg/cu m.

3. Interferences

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.029-0.17 mg/cu m was 0.086. This value corresponds to a standard deviation of 0.009 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 98.8% was determined for the collecting medium; thus no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method--the average recovery from the filters was 101.3%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

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

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37-mm, 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

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 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 3% OV-101 on 100/120 mesh Supelcoport.

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

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.

6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Anhydrous ether, reagent grade

7.2 Triorthocresyl phosphate, reagent grade

7.3 Purified hydrogen

7.4 Prefiltered, compressed air

7.5 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 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 be passed through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 100 liters is recommended but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.5 Turn the pump on and begin sample collection. During the sampling period the pump rotameter should be observed frequently. It is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air; the 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 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. At least one blank per 10 samples should be submitted.

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

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers.

2. Transfer filter to the jar and pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.

3. Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.

8.4.2 GC Conditions. Follow instrument manufacturer's recommendation on optimum gas flow rates. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (50 psig) Nitrogen carrier gas flow
2. 70 ml/min Hydrogen gas flow to detector
3. 150 ml/min Air flow to detector
4. 250°C injector temperature
5. 250°C detector temperature
6. 220°C column temperature

8.4.3 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 technique.

8.4.4 Measurement of area. The total area of the 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 in Section 9.

8.5 Determination of Sample Recovery

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

8.5.2 Procedure for determining recovery. A known amount of a standard stock solution of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) have been dosed accordingly using a solution of triorthocresyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were ther extracted and analyzed as described in Section 8.4. The average recovery value obtained over all levels was 101% and as such no correction factor has been used in the determination of the "true" values.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. The triorthocresyl phosphate liquid is viscous and is difficult to measure accurately with a microliter syringe. Thus, it is suggested that a stock solution of triorthocresyl phosphate in ether be prepared by weighing triorthocresyl phosphate and diluting to volume. This stock solution can be used for the preparation of other calibration standards. Prepare calibration standards fresh daily. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC

conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

NOTE: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and therefore it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 10.0 ml ether and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

11. Reference

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

Triphenyl Phosphate

Analyte:	Triphenyl Phosphate	Method No.:	S210
Matrix:	Air	Range:	1.25-6.99 mg/cu m
OSHA Standard:	3.0 mg/cu m	Precision ($\overline{CV}_T$):	0.066
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date:	11/21/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and extracted with ether.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).

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

2. Range and Sensitivity

2.1 This method was validated over the range of 1.25-6.99 mg/cu m at an atmospheric temperature and pressure of 24°C and 759 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.5-9 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 900-microgram sample.

2.2 The upper limit of the range of the method is dependent on the filtration capacity 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 triphenyl phosphate aerosol was found to be 99% when sampled for 66 minutes at 1.5 liters per minute from a test atmosphere containing 7.0 mg/cu m.

3. Interferences

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 1.25-6.99 mg/cu m is 0.066. This value corresponds to a standard deviation of 0.2 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 99.3% was determined for the collecting medium; thus no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery from the filters was 99.1%. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

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

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 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.

6.2 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 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.

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

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.

6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Anhydrous ether, reagent grade

7.2 Triphenyl phosphate, reagent grade

7.3 Purified hydrogen

7.4 Prefiltered, compressed air

7.5 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 filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection ar 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 be passed through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 100 liters is recommended but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least +5%.

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

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

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of 10 samples submit one filter which is subjected to exactly the same handing as for the samples except that no air is drawn through it. Label this as a blank.

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

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers.

2. Transfer filter to the jar and pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.

3. Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.

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

1. 50 ml/min (50 psig) Nitrogen carrier gas flow
2. 20 ml/min Hydrogen gas flow to detector
3. 150 ml/min Air flow to detector
4. 250°C injector temperature
5. 250°C detector temperature
6. 210°C column temperature

8.4.3 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 technique.

8.4.4 Measurement of area. The total area of the 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 in Section 9.

8.5 Determination of Sample Recovery

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

8.5.2 **Procedure for determining recovery.** A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly using a solution of triphenyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 99% and as such no correction factor has been used in the determination of the "true" values.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

NOTE: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and therefore it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 10.0 ml ether and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

μg sample = μg found in sample filter
μg blank = μg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample.

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (Liter)}}$$

11. Reference

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

1,1-Dichloro-1-nitroethane

Analyte:	1,1-Dichloro-1-nitroethane	Method No.:	S213
Matrix:	Air	Range:	27-115 mg/cu m
OSHA Standard:	10 ppm (60 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/21/75

1. Principle of the Method

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, capped 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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 27-115 mg/cu m at an atmospheric temperature and pressure of 23°C and 763 mm Hg, using a 17-liter sample. Under the conditions of recommended sample size (15 liters) the probable useful range of this method is 6-180 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.7-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 18 mg of analyte when a test atmosphere containing 116 mg/cu m of analyte in air was sampled at 0.79 liter per minute for 193 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the 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 as 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 27-115 mg/cu m was 0.055. This value corresponds to a 3.3 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 1.2% 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.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can

be eliminated by altering chromatographic conditions. The 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 and/or by using another column.

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 ±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 petroleum based charcoal. 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% SP-1000 stationary phase on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,1-Dichloro-1-nitroethane, spectroquality.

7.3 Undecane, or other suitable internal standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 same 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 backup 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 of 15 liters is recommended. This can be accomplished by sampling for 15 minutes at a rate of 1.0 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 15-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon sulfide 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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

11.1 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.

Ethylene Glycol Dinitrate and/or Nitroglycerin

Analyte:	EGDN and/or NG	Method No.:	S216
Matrix:	Air	Range:	0.51-1.84 mg/cu m -EGDN 0.56-3.21 mg/cu m -NG
OSHA Standard:	0.2 ppm (1.0 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.089 - EGDN 0.104 - NG
Procedure:	Adsorption on Tenax-GC resin, desorption with ethyl alcohol GC/ECD	Validation Date:	11/21/75

1. Principle of the Method

1.1 A known volume of air is drawn through a tube containing Tenax-GC resin to adsorb the ethylene glycol dinitrate (EGDN) and/or nitroglycerin (NG) present.

1.2 The Tenax-GC resin in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with ethyl alcohol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph with an electron capture detector.

1.4 The area of the resulting peak is determined and compared with corresponding areas obtained fron injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.51-1.84 mg/cu m for ethylene glycol dinitrate and 0.56-3.21 mg/cu m for nitroglycerin at an atmospheric temperature and pressure range of 22-24°C and 755-766 mm Hg, using a 15-liter sample. Under the conditions of sample size (15 liters) the probable useful range of this method for these nitrate esters is 0.2-3 mg/cu m provided that the GC analysis is conducted such that proper dilutions and aliquoting are made to ensure that the linear range of the ECD response is not exceeded. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the Tenax-GC resin tube. This capacity can vary with the concentrations of analyte and other substances in the air. Breakthrough studies indicated that the first section of the Tenax-GC resin tube was found to hold at least 0.4 mg of EGDN when a test atmosphere containing 1.6 mg/cu m of EGDN in

air was sampled at 1.1 liters per minute for 240 minutes; the resin tube was also found to hold at least 0.5 mg of NG when a test atmosphere containing 2.7 mg/cu m of NG on air was sampled at 1.1 liters per minute for 240 minutes. At that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

The resin tube consists of two sections of Tenax-GC resin separated by a section of silylated glass wool. (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 The adsorptive capacity of Tenax-GC resin is not severely affected by water vapor. Experimental tests indicate that the retention of EGDN and NG by the sorbent tubes is not significantly different when samples are taken from atmospheres of low and high relative humidities (Reference 11.1).

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 as 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.

3.5 Ethylene glycol mononitrate, if present in high concentration relative to that of EGDN, produces a gas chromatographic peak that tails into the EGDN peak. This interference, although troublesome, does not prohibit a satisfactory analysis of EGDN. The combined selectivity of Tenax-GC and electron capture detection practically eliminates other interferences.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method for EGDN in the range of 0.51-1.80 mg/cu m was 0.0890 and was 0.104 for NG in the range of 0.56-3.2 mg/cu m. These $\overline{CV}_T$ values correspond to a standard deviation of 0.09 and 0.10 mg/cu m at the OSHA standard level for EGDN and NG respectively. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 A collection efficiency of 100% was determined for the collection medium at the 2X OSHA standard test level for a sample size of 15 liters for each nitrate ester; thus, no bias was introduced in the sample collection step. Any bias due to desorption efficiency has also been controlled by correcting the found values for the appropriate DE factor with an average of 0.92 and 0.98 for EGDN and NG respectively over the concentration range equal to 0.5 to 2X OSHA standard for a 15-liter sample. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

4.3 In a separate experimental study (Reference 11.1), the average recovery of EGDN from vapor samples at concentrations of 0.27 to 3.93 mg/cu m in 30 to 90-liter samples was 104% and that of NG was 102% at a concentration of 0.28 mg/cu m in 60-liter samples.

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.

5.2 The method can be applied for a wide range of sample sizes. However, repeated dilutions of the ethanol extract may be necessary to bring the amount of sample injected into the proper range for the electron capture detector (Reference 11.1).

5.3 The principal difficulties are those associated with the use of electron capture detection. They include the limited linear range of electron capture detectors and operating variables such as the effects of column bleed, moisture, and oxygen. The effects of these variables may be minimized by analyzing standards at the same time as samples. The electron capture is about 500 times as sensitive to the nitrate esters as a hydrogen flame ionization detector, and it provides a substantial advantage in specificity. The election capture detector is highly sensitive to electrophillic substances such as halogenated compounds. The presence of large amounts of these materials may overload the detector and special sample handling and precleaning may be necessary before the analysis of NG or EGDN can be carried out.

5.4 Another 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 resin tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.5 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 ±5% at the recommended flow rate. (Reference 11.2)

6.2 Resin tubes: glass tube with both ends flame-sealed, 7 cm long with 7-mm O.D. and 5-mm I.D., containing 2 sections of 35/60 mesh Tenax-GC resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the outlet end of the tube and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

6.3 Gas chromatograph equipped with an electron capture detector.

6.4 Column (2-1/2 ft x 1/4 inch glass, 2-mm I.D.) packed with 10% OV-17 stationary phase on 60/80 mesh Gas Chrom Q.

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

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

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

6.8 Pipets: 2-ml, delivery type.

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

7. Reagents

7.1 Ethyl alcohol, absolute

7.2 Standard solutions of EGDN and NG (refer to Section 9.0)

7.3 Purified Argon/methane (95:5), carrier gas

7.4 Tenax-GC, 35/60 mesh (distributed by Applied Science Laboratories Inc., State College, Pa.)

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. Particular attention should be paid to the cleaning of the microliter syringe used for sample injection with ethanol.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative Tenax-GC resin tube (sorbent 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 sorbent is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The sorbent tube should be placed in a vertical position with the larger section of sorbent pointing up during sampling to minimize channeling of EGDN and NG through the sorbent tube.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the sorbent tube. This is particularly important with the nitrate esters since they are strongly sorbed on most surfaces, including glass.

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

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

8.3.7 The sorbent tubes should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube for every 10 samples 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 sorbent tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of glass wool 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 and Dilution. Prior to analysis, 2.0 ml of ethyl alcohol is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

For the analysis of EGDN, a sample dilution of 1:5 should be done after complete desorption (30 minutes) because of the limited and narrow linear range of ECD response for EGDN. Some ECD units are available with wider linear dynamic range; if this type of instrument is used, this sample dilution may not be necessary.

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

1. 75 ml/min (60 psig) 95% Argon/Methane carrier gas flow
2. 45 ml/min (60 psig) Scavenger gas flow to detector
3. 160°C injector temperature
4. 280°C manifold temperature (detector)
5. 125°C column temperature

Note: Avoid operating the column above 150°C because decomposition of NG may occur (Reference 11.1); for this reason, also avoid injector temperatures above 160°C.

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 blowback 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. Two 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 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1-2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. 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 technique.

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 may vary from one laboratory to another and also from one batch of Tenax-GC resin 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 resin is used.

8.5.2 Procedure for determining desorption efficiency. An amount of the resin equivalent to that present 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 resin must be from the same batch as that used in obtaining the samples and can be obtained from unused resin tubes. The open end is capped with Parafilm. A known amount of a solution of EGDN and/or NG** in ethyl alcohol is injected directly into the resin with a microliter syringe, and the tube is capped with more Parafilm. Alternatively a 5-ml vial with Teflon-faced septum, may be used in place of the glass tube.

**The standard stock solution of EGDN and NG may be used for these studies. Do not use more than a 15-µl aliquot of the analyte solution in ethanol.

Six tubes at each of three concentration levels (0.5, 1 and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 15-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the resin. 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 2.0 ml of ethyl alcohol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the resin. 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

9.1 If pure NG and EGDN are available, standard solutions in ethanol may be prepared and analyzed under the same gas-chromatographic conditions and during the same time period as the unknown samples. In the validation studies conducted for this method, standard solutions of EGDN and NG in ethyl alcohol were provided upon request by a dynamite manufacturer. Reference 11.5 also cites the following materials which can be obtained from manufacturers of nitrate ester products for the preparation of standards.

9.1.1 A sample of analyzed dynamite containing EGDN but no NG may be obtained from a dynamite manufacturer. Since dynamite is a heterogeneous material, care must be taken to obtain a representative sample.

9.1.2 Pharmaceutical-grade sublingual NG tablets may be obtained from wholesale drug dealers. These tablets are manufactured to meet United States Pharmacopeia specifications, which require that the actual NG content be between 80 and 112% of the stated value. The actual NG content of a specific lot of tablets may be obtained from the manufacturer. For use, the tablets

are weighed, crushed, and extracted with ethanol, the solution is filtered and diluted to a fixed volume and aliquots are injected.

9.1.3 An alternate source is a material of a known NG content called "Nitroglycerin Lactose Trituration", provided by a pharmaceutical manufacturer. This material is used for quality control in the manufacture of NG tablets.

9.2 It is convenient to express concentration of standards in terms of µg per 2.0 ml of ethyl alcohol, because samples are desorbed in this amount of ethyl alcohol. A series of standards, varying in concentration over the range of interest, is prepared from the standard stock solution and analyzed under the same GC conditions and during the same time period as the unknown sample. It is important to note that the concentration range used for calibration must be within the linear range of ECD response; this range is narrow for EGDN.

9.3 Calibration curves are established by plotting concentration in µg per 2.0 ml versus peak area.

9.4 Standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in ECD response. Moreover, since the ECD response is very sensitive to changes in the detector standing current, the standards must be carefully interspersed with the samples during the analysis.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. For NG, no volume corrections are needed because the standard curve is based on µg per 2.0 ml ethyl alcohol and the volume of sample injected is identical to the volume of the standards injected. For EGDN, however, multiply by the appropriate dilution factor to obtain the total µg of EGDN in the sample.

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

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

where:

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

A similar procedure is followed for the backup section.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight of EGDN and/or NG 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 µg/sample.

$$\text{Corrected µg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 If unusual temperatures and pressures were encountered during sampling, convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = Volume of air in liters at 25°C and 760 mm Hg
V = Volume of air in liters as measured
P = Barometric pressure in mm Hg
T = Temperature of air in °C

10.6 The concentration of each compound in the air sampled may be expressed in mg/cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{V_s}$$

10.7 Concentrations in mg/cu m may be converted to parts per million (ppm) by volume under standard conditions by the following equations:

$$\text{For NG, ppm} = \text{mg/cu m} \times \frac{24.45}{MW} = \text{mg/cu m} \times 0.108$$

$$\text{For EGDN, ppm} = \text{mg/cu m} \times \frac{24.45}{MW} = \text{mg/cu m} \times 0.161$$

where:

24.45 = molar volume (liter per mole) at 25°C and 760 mm Hg
MW = molecular weight (227.09 g/mole for NG and 152.07 g/mole for EGDN)

11. References

11.1 Final Report, NIOSH Contract No. HSM-99-73-63, "Sampling and Analysis of Four Organic Compounds Using Solid Sorbents," 1974.

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.

11.4 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere." Amer. Ind. Hyg. Ass. J., 31, 225 (1970).

11.5 P&CAM 203, "Nitroglycerin and Ethylene Glycol Dinitrate (Nitroglycol) in Air."

Nitrobenzene

Analyte:	Nitrobenzene	Method No.: S217
Matrix:	Air	Range: 3.11-12.45 mg/cu m
OSHA Standard:	1 ppm (5 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.058
Procedure:	Adsorption on silica gel, desorption with methanol, GC	Validation Date: 11/21/75

1. Principle of the Method

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 methanol.

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 3.11-12.45 mg/cu m at an atmospheric temperature and pressure of 23°C and 765 mm Hg, using a 55-liter sample. Under the conditions of sample size (55 liters) the probable useful range of this method is 0.5-15 mg/cu m. 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 2.78 mg of analyte when a test atmosphere containing

12.45 mg/cu m of analyte in air was sampled at 0.930 liter per minute for 240 minutes; at that time the concentration of nitrobenzene in the effluent was less than 5% of that in the influent. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 3.11-12.45 mg/cu m was 0.058. This value corresponds to a 0.29 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 [1].

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.6% 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 Section 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.

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 ±5% at the recommended flow rate. (Reference 11.1)

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 long X 1/8-in O.D. 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: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Methanol, reagent grade.

7.2 Nitrobenzene, 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 $\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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

8.3.9 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 methanol is pipetted into each sample container. The sample is desorbed 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. 245°C injector temperature
5. 275°C manifold temperature (detector)
6. 160°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 reporducibility 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 a hexane solution of nitrobenzene containing 60 mg/ml is injected directly into the silica gel with a microliter syringe. Cap the silica gel tube 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 60-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 methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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 methanol, because samples are desorbed in this amount of methanol. The density of the analyte is used to calculate mgs from 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 methanol 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.

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

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. Reference

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

p-Nitrochlorobenzene

Analyte:	p-Nitrochlorobenzene	Method No.: S218
Matrix:	Air	Range: 0.428-2.75 mg/cu m
OSHA Standard:	1 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.103
Procedure:	Adsorption on silica gel, desorption with methanol, GC	Validation Date: 11/21/75

1. Principle of the Method

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 methanol.

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 0.428-2.75 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 50-liter sample. Under the conditions of sample size (50 liters) the probable useful range of this method is 0.1-3 mg/cu m. 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 2.15 mg of analyte when a test atmosphere containing

9.94 mg/cu m of analyte in air was sampled at 0.90 liter per minute for 240 minutes; at that time the concentration of p-nitrochlorobenzene in the effluent was less than 5% of that in the influent. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 0.428-2.75 mg/cu m was 0.103. This value corresponds to a 0.10 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 was determined for the collection medium, thus, no bias was introduced in the sample collection step. There is no bias in the sampling and analytical method for which a desorption efficiency 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. 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.

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 ±5% at the recommended flow rate. (Reference 11.1)

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 long X 1/8-in O.D. 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 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 Methanol, reagent grade.

7.2 p-nitrochlorobenzene, reagent grade.

7.3 n-Hexane, reagent grade.

7.4 Benzene, reagent grade.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

7.7 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 nearer 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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

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

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file 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 methanol 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. 180°C injector temperature
5. 260°C manifold temperature (detector)
6. 155°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 volume of solution containing 125 mg of p-nitrochlorobenzene in 2 ml of benzene and enough hexane to make 10 ml of solution is injected directly into the silica gel with a microliter syringe.

Cap the silica gel tube 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 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 methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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 methanol, because samples are desorbed in this amount of methanol. 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 methanol and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

11. Reference

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

Nitrotoluene

Analyte:	Nitrotoluene	Method No.: S223
Matrix:	Air	Range: 11.35-58.2 mg/cu m
OSHA Standard:	5 ppm (30 mg/cu m) - skin	Precision ($\overline{CV}_T$): 0.062
Procedure:	Adsorption on silica gel, desorption with methanol, GC	Validation Date: 12/19/75

1. Principle of the Method

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 methanol.

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 for o-nitrotoluene over the range of 11.35-58.2 mg/cu m at an atmospheric temperature and pressure of 23°C and 765 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable range of this method is 0.3-90 mg/cu m. 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 2.5 mg of analyte when a test atmosphere containing

52.1 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 256 minutes; at that time the concentration of nitrotoluene in the effluent was less than 5% of that in the influent. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 total analytical and sampling method in the range of 11.35-58.2 mg/cu m was 0.063 for o-nitrotoluene. This value corresponds to a 1.9 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 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step. There is no bias in the sampling and analytical method for which a desorption efficiency correction was made. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

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 ±5% at the recommended flow rate. (Reference 11.2)

6.2 Silica gel tubes: glass tube with both ends flame sealed, [illegible] 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 long x 1/8-in O.D. stainless steel) packed with 5% SE-30 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 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 Methanol, reagent grade.

7.2 o-Nitrotoluene, m-nitrotoluene, and p-nitroluene, all 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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

8.3.9 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 methanol 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. 150°C injector temperature
5. 250°C manifold temperature (detector)
6. 90°C column temperature

If the three isomers are present in the sample, the above GC conditions can be used to separate them.

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 the nitrotoluene present (containing 150 mg/ml) is injected directly into the silica gel with a microliter syringe. Cap the silica gel tube 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 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 methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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 10.1.4 to correct for adsorption losses.

8.5.3 A desorption efficiency curve should be prepared for each isomer of nitrotoluene that is detected in the sample (Section 9.4).

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml methanol, because samples are desorbed in this amount of methanol. 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.

Separate standards should be prepared for each isomer of nitrotoluene, and a calibration curve established for each.

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 For each isomer, determine the mg/sample as follows.

10.1.1 Read the weight, in mg, corresponding to each peak area from the standard curve for that isomer. No volume corrections are needed, because the standard curve is based on mg/1.0 ml methanol and the volume of sample injected is identical to the volume of the standards injected.

10.1.2 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.

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

10.1.4 Read the desorption efficiency from the curve for that isomer (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.

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

10.2 Add the corrected mg/sample for each isomer to obtain the total corrected mg/sample.

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

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

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

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

Tetranitromethane

Analyte:	Tetranitromethane	Method No.:	S224
Matrix:	Air	Range:	2.70-11.5 mg/cu m
OSHA Standard:	1 ppm (8 mg/cu m)	Precision ($\overline{CV}_T$):	0.076
Procedure:	Collection in ethyl acetate/impingers, GC/alkali-FID	Validation Date:	12/19/75

1. Principle of the Method

1.1 A known volume of air is drawn through impingers containing ethyl acetate to collect the tetranitromethane.

1.2 An aliquot of the sample solution is injected into a gas chromatograph equipped with an alkali-flame ionization detector.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 2.70-11.5 mg/cu m at an atmospheric temperature and pressure of 19°C and 763 mm Hg, using a 250-liter sample. Under the conditions of sample size (250 liters) the probable useful range of this method is 1-16 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4-mg sample.

2.2 The upper limit of the range of the method is dependent on the collection efficiency. The method is capable of measuring concentrations higher than that noted in Section 2.1 provided the collection efficiency is adequate.

3. Interference

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

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2.7-11.5 mg/cu m was 0.076. This value corresponds to a 0.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 0.895 $\pm$0.010 was determined for the collecting medium at an analyte concentration equal to 2X OSHA standard level. The collection efficiency was used as a correction factor to determine the concentration of the air sampled in order to compensate for any bias in the sampling method. There was no apparent bias in the analytical method-the average recovery based on 18 spiked samples was 98%. 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

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

6. Apparatus

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

6.1.1 A glass standard midget impinger.

6.1.2 A calibrated personal sampling pump suitable for sampling at 1 liter per minute for 250 minutes. The pump must be accurate to within $\pm$5% at the recommended flow rate. The sampling pump is protected from splashover or water condensation by a 2-inch 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 or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Gas chromatograph equipped with an alkali-flame ionization detector.

6.3 Column (6-ft x 1/4 in glass, 2 mm ID) packed with 3% OV-101 stationary phase on 100/120 mesh Supelcoport AW-DMCS. Do not use metal columns.

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

6.5 Volumetric flasks: 25 ml.

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

6.7 Polyethylene vials - 20 ml with screw caps.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Ethyl acetate, Nanograde

7.2 Tetranitromethane

7.3 Purified helium

7.4 Purified 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 Sampling Pumps. Each pump should be calibrated by using an integrated volume meter (6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pipet 15 ml of ethyl acetate into each midget impinger.

8.3.2 Connect the midget impinger in series with the 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 impinger. The impinger must be maintained in a vertical position during sampling.

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 250 liters is recommended. Periodically fill impingers with ethyl acetate and do not allow solvent level to go down below 10 ml.

8.3.4 After sampling, the impinger top can be removed and cleaned. Tap the stems gently against the inside walls of the impinger bottoms to recover as much of the sampling solution as possible. Transfer the sample solution into the 20-ml polyethylene vial. Rinse the stem of the impinger top and bottom with 1-2 ml of ethyl acetate and transfer rinsing into the polyethylene vial. Repeat rinsing process 2-3 times to ensure complete sample transfer.

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 shipping cases designed by NIOSH should be used to ship the samples.

8.3.7 A "blank" impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this impinger. Submit one "blank" for every 10 samples collected.

8.4 Analysis of Samples

8.4.1 Preparation for analysis. Transfer sample solution from the polyethylene vial to a 25-ml volumetric flask and dilute to volume with ethyl acetate. If an automatic sample injector is used, transfer the samples to the associated sample vials after the dilution to 25 ml.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph with an alkali-FID are:

1. 40 ml/min (60 psig) helium carrier gas flow
2. 40 ml/min (24 psig) hydrogen gas flow to detector
3. 280 ml/min (50 psig) air flow to detector
4. 150°C injector temperature
5. 175°C detector temperature
6. 40°C column temperature

8.4.3 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 3-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 2.9-3.0 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.

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

8.5 Determination of Analytical Method Sample Recovery

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

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to 15 ml of ethyl acetate and stored for at least one day in the polyethylene vials. The solutions are then analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 250-liter sample at

the selected level has been used for the recovery studies. Six samples at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been prepared accordingly. A parallel blank solution of ethyl acetate was also treated in the same manner except that no sample was added to it. All solutions were stored for 5 days and analyzed as described in Section 8.4. The average recovery values obtained were at least 98% and as such no recovery correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in mg found in the ethyl acetate solution divided by the weight in mg added, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Found}}{\text{Weight (mg) Added}}$$

9. Calibration and Standards

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

10. Calculations

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

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

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

where:

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

10.3 Divide the total weight by the analytical method recovery and a collection efficiency of 0.90 to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery} \times 0.90}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

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

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

where:

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

11. Reference

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

Tetryl

(2,4,6-Trinitrophenylmethylnitramine)

Analyte:	Tetryl	Method No.:	S225
Matrix:	Air	Range:	0.882-4.51 mg/cu m
OSHA Standard:	1.5 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.065
Procedure:	Filter collection, colorimetric	Validation Date:	12/19/75

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 The filters are extracted with N,N-diethylethanolamine.

   1.3 The absorbance of the resulting reddish-brown solution is read at 420 nm as a quantitative measure of tetryl.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.882-4.51 mg/cu m at an atmospheric temperature and pressure of 23°C and 770 mm Hg. The probable range of the method is 0.15 -4.5 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 to extend the upper limit of the range.

   2.2 A concentration of 0.15 mg/cu m of tetryl can be determined in a 100-liter air sample based on a 0.05 absorbance using a 1-cm cell.

3. Interferences

   Other nitro aromatic compounds may interfere if they produce a color when dissolved in N,N-diethylethanolamine. A number of nitro compounds are capable of yielding a color in many organic solvents. Trinitrotoluene (TNT) gives a red-violet color in N,N-diethylethanolamine, which gradually changes to a yellow-red color (Reference No. 2). Since TNT would likely be collected on the filter if it is present in the air, it would give a positive interference and result in a high reading for tetryl.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.882-4.51 mg/cu m was 0.065. This value corresponds to a 0.098 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be fo- in Reference 11.3.

4.2 A collection efficiency of 0.985, standard deviation of 0.004, (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is 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 samples, collected on filters, are analyzed by means of a quick, instrumental method.

5.2 The color developed has the greatest absorption maximum, between 2.5 to 3.5 hours after addition of N,N-diethylethanolamine.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of tetryl has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate polystyrene 37-mm 3-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Spectrophotometer. This instrument should be capable of measuring the developed color at 420 nm.

6.4 Matched glass cells or cuvettes, 1-cm path length.

6.5 Assorted laboratory glassware -- pipets, volumetric flasks, graduated cylinders of appropriate capacities, glass screw cap bottles with Teflon-lined caps.

6.6 Tweezers.

6.7 Wrist action shaker.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Tetryl, reagent grade.

7.2 Benzene, reagent grade.

7.3 Tetryl standard solution. Weigh accurately 0.375 g of tetryl and dissolve in benzene in a 25-ml volumetric flask. Bring volume in the flask to the mark. The concentration of this solution is 15 mg/ml.

7.4 N,N-Diethylethanolamine, 99%. Caution must be taken when handling N,N-diethylethanolamine, since it is very toxic.

8. Procedure

8.1 Cleaning of equipment. No specialized cleaning of glassware is required.

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

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

8.3.9 The filter should be removed from the cassette filter holder within one hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.

8.3.10 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 Each sample is analyzed separately.

8.4.2 Pipet 10 ml of N,N-diethylethanolamine into each screw cap bottle and cap each bottle.

8.4.3 Shake each bottle for 10 minutes on a wrist action shaker.

8.4.4 Transfer the colored solution to a new screw cap bottle and allow each sample to stand for 2.5-3.5 hours.

8.4.5 Read each sample using a 1-cm cell at 420 nm in the spectrophotometer against a blank prepared from N,N-diethylethanolamine.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the three levels with appropriate amounts of the standard solution described in Section 7.3. This corresponds to the amount of tetryl collected in a 100-liter sample at the 0.5X, 1X, and 2X levels, respectively. Allow the filters to dry and place each filter in a screw cap bottle and allow to stand overnight. The analyte is then extracted from the filter and analyzed as described in Section 8.4.

A parallel blank filter is also treated in the same manner except that no sample is added to it.

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

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

9. Calibration and Standards

9.1 Into 5 screw cap bottles, pipet 10 ml of N,N-diethylethanolamine.

9.2 Carefully pipet 3, 7, 15, and 25 microliters of the standard solution (Section 7.3) into each bottle. Process one bottle as a blank.

9.3 Cap each bottle with a Teflon-lined cap. Shake the jars on a wrist action shaker for 10 minutes. Allow samples to stand for 2.5-3.5 hours.

9.4 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.

9.5 Read the blank, prepared from N,N-diethylethanolamine, and then each sample at 420 nm.

9.6 Construct a calibration curve by plotting absorbance against micrograms tetryl in the colored developed solution.

10. Calculations

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

10.2 Determine from the calibration curve (Section 9.6) the µg of tetryl present in each sample.

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

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

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Goldman, F. H. and D. E. Rushing, "The Estimation of Minute Amounts of Tetryl in the Atmosphere," Journal of Industrial Hygiene and Toxicology, 25 (5), (1943), 195.

11.2 Goldman, F. H., and D. E. Rushing, "Diethylaminoethanol as a Reagent for Detection and Colorimetric Determination of Small Amounts of Trinitrotoluene in Air," J. Ind. Hyg. Toxicol., 25, (1943), 164.

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

n-Propylnitrate

Analyte:	n-Propylnitrate	Method No.:	S227
Matrix:	Air	Range:	50-209 mg/cu m
OSHA Standard:	25 ppm (110 mg/cu m)	Precision ($\overline{CV}_T$):	0.054
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/19/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 50-209 mg/cu m at an atmospheric temperature and pressure of 21°C and 771 mm Hg, using a 70-liter sample. Under the conditions of sample size (70 liters) the probable useful range of this method is 11-330 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 23-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 24 mg of analyte when a test atmosphere containing 209 mg/cu m of analyte in air was sampled at 0.79 liters per minute for 143 minutes; breakthrough was observed at this time, i.e., the concentration of analyte 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 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 as 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 50-209 mg/cu m was 0.054. This value corresponds to a 5.9 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 0.5% 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.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can

can be eliminated by altering chromatoagraphic 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 and/or by using another column.

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 ±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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 80/100 mesh Chromosorb W-AW.

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, graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 n-Propylnitrate, reagent grade.

7.3 Decane, or other suitable internal standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 backup 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 70 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rates 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 85°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 70-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

11.1 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.

Analyte:	Arsine	Method No.:	S229
Matrix:	Air	Range:	0.094 - 0.404 mg/cu m
OSHA Standard:	0.05 ppm (0.2 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on charcoal, desorption with 0.01 M nitric acid, Flameless atomic absorption	Validation Date:	6/6/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the arsine vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 0.01 M nitric acid.

1.3 The desorbed sample is analyzed by flameless atomic absorption spectroscopy in a high temperature graphite atomizer.

1.4 The area of the resulting absorption peak at 193.7 nm is determined and compared with areas of absorption peaks obtained from injection of standards.

1.5 The samples must be carefully interspersed between calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.094 - 0.404 mg/cu m at an atomospheric temperature and pressure of 27.6°C and 761 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters), the probable useful range of this method is 0.04 - 0.60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-microgram sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 0.021 mg of analyte when a test atmosphere containing

0.405 mg/cu m of analyte in air was sampled at 0.22 liters per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. (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. The collection efficiency of arsine is dependent on sampling rate; the sampling rate is limited to 0.2 liters per minute or less, since higher flow rates may result in low collection efficiency.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, arsine vapors may not be trapped efficiently.

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 Other arsenic compounds which exist as vapors will interfere with the analysis. It is expected that interference from particulate arsenic compounds may be eliminated by putting a filter cassette before the charcoal tube.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.094 - 0.404 mg/cu m was 0.056. This value corresponds to a 0.011 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 On the average, the concentrations obtained at the OSHA standard level, using the overall sampling and analytical method, were 3.3% 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.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal. The tubes are analyzed by means of an instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When 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 ± 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 Atomic absorption spectrophotometer having a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and background corrector accessory. The Perkin Elmer 503 with the Model 2100 HGA is one example. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 193.7 nm wavelength.

6.4 The arsenic radiation source may be either an electrodeless discharge lamp or a hollow cathode lamp. The former is recommended because it is a brighter source.

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

6.6 Volumetric flasks: 10-ml and other convenient sizes for making standards.

6.7 Pipets: Assorted sizes for making standards.

6.8 Eppendorff automatic pipettor with disposble plastic pipets for accurately injecting 50 microliter sample aliquots into the graphite furnace tube.

6.9 Assorted glassware.

6.10 Ultrasonic agitator.

7. Reagents

All chemicals must be ACS reagent grade or better.

7.1 Nitric acid, 0.01 M

7.2 Nitric acid, 0.1 M

7.3 Distilled water

7.4 High purity argon

7.5 Arsenic standards

7.5.1 Arsenic standard stock solution, 1000 pm. Stock solutions may be purchased from reliable suppliers (such as Fisher Scientific) or they may be prepared by dissolving either 1.000 g of metallic arsenic or 1.320 g of arsenous oxide (As_2O_3) in 0.1 M nitric acid and diluting to 1000 ml with 0.1 M nitric acid.

7.5.2 Dilute arsenic stock solution (10 µg/ml). Dilute 1.0 ml of the 1000 ppm standard to 100 ml with 0.01 M nitric acid. Prepare fresh daily.

7.5.3 Working standards. Prepare by diluting 0.5, 1.0, 2.0, 4.0 and 5.0 ml of the dilute arsenic stock solution (Section 7.5.2) to 100 ml with 0.01 M nitric acid. These solutions contain 0.05, 0.10, 0.20, 0.40 and 0.50 µg/ml. Prepare solutions fresh daily.

8. Procedure

8.1 Cleaning of Equipment. All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is cleaned with hot, concentrated nitric acid and thoroughly rinsed with tap water followed by 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 assocated 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 backup 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 of 10 liters is recommended. Sample at a rate of 0.2 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 charcoal tubes should be packed tightly and padded before they are shipped to minimize the tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file 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 a 2-ml stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 10.0 ml of nitric acid is pipetted into each sample container. Desorption should be done for 30 minutes with ultrasonic agitation. Tests indicate that this is adequate if the sample is agitated in an ultrasonic agitator during this period. In the desorption of the backup section, only 1.0 ml of 0.01 M nitric acid is used for increased sensitivity.

8.4.3 Spectrometric measurements.

1. The instrumental parameters for source power, background corrector, and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying and atomization should be established in accordance with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of arsenic during these steps.

2. Inject a 50-microliter aliquot of the sample solution into the graphite tube using an automatic pipettor with disposable plastic tips.

3. A minimum of duplicate analyses per sample should be done.

4. To obtain reliable results, samples must be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, ... etc.

NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak areas, it must be rejected and replaced because results so obtained are not reliable.

8.4.4 Measurement of Area. The area of the absorption peak is measured by some suitable form of area measurement such as a planimeter or an electronic integrator. The integrator accessory (10-second integration) of the Perkin Elmer Model 503 has been used successfully for this purpose. Note that peak height measurements will not give precise nor reliable results.

8.5 Determination of Desorption Efficiency

It is anticipated that it would be troublesome to carry out desorption efficiency tests because of the difficulty involved in accurately adding a known amount of arsine gas to the charcoal. Thus, it is recommended that the recovery values derived from the experimental studies conducted be used in order to determine the concentration of the air sampled. The correction factors are 0.90 for the 0.5X and 1.0 for the 1X and 2X OSHA standard for a 10-liter sample collected at a flow rate of 0.2 liters per minute.

9. Calibration and Standards

9.1 Prepare a series of working standards containing 0.5 to 6.0 mg of arsenic in 10 ml of 0.01 M nitric acid. These standards should be prepared fresh each time. Refer to Section 7.5.

9.2 To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor determined from the response of the calibration standard.

10.2 Convert micrograms arsenic to micrograms arsine using molecular weight ratio, 78/75 = 1.04.

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

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

where:

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

10.4 Add the amount present in the front and backup sections of the sample tube to determine the total weight in the sample.

10.5 Divide the total weight in μg found by the correction factor as discussed in Section 8.5; use 0.90 for the 0.5X and 1.0 for the 1 and 2X OSHA standard.

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

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.5)}}{\text{Air Volume Sampled (Liters)}}$$

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

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

where:

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

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-75.

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

Analyte:	Hydrazine	Method No.:	S237
Matrix:	Air	Range:	0.589-3.44 mg/cu m
OSHA Standard:	1 ppm (1.3 mg/cu m)-skin	Precision ($\overline{CV}_T$):	0.094
Procedure:	Bubbler collection, colorimetric	Validation Date:	12/19/75

1. Principle of the Method (Reference 11.1)

1.1 Hydrazine is collected in a midget bubbler containing 0.1 M hydrochloric acid.

1.2 The resulting solution is made alkaline with 1.2 M sodium hydroxide, and the solution is then reacted with p-dimethylaminobenzaldehyde to form an orange colored complex.

1.3 The solution is allowed to stand for a half hour before addition of glacial acetic acid.

1.4 The strong absorption maximum at 480 nm is used as a quantitative measure of hydrazine.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.589-3.44 mg/cu m, at an atmospheric temperature and pressure of 22°C and 763 mm Hg. The probable range of the method is 0.02-4.0 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 glacial acetic acid prior to color development to extend the upper limit of the range.

2.2 A concentration of 0.013 mg/cu m of hydrazine in a 100-liter air sample gives a 0.015 absorbance using a 1-cm cell.

3. Interferences

3.1 Hydrazine derivatives may interfere with the method.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.589-3.44 mg/cu m was 0.094. This value corresponds to a 0.12 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 0.997, standard deviation of 0.002, (essentially 1.00) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

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

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

6. Apparatus

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

6.1.1 A glass, midget bubbler with a stem which has a fritted glass end and contains 10 ml of 0.1 M hydrochloric acid (Section 7.1). The fritted end should have porosity approximately equal to that of Corning EC (170-220 micron maximum pore diameter).

6.1.2 A pump suitable for sampling at least 1.0 liter per minute. (Reference 11.2). 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 must be capable of measuring the absorbance of the developed color at 480 nm.

6.3 Matched glass cells or cuvettes, 1-cm path length.

6.4 Assorted laboratory glassware--pipets, volumetric flasks, large test tubes, and graduated cylinders of appropriate capacities.

7. Reagents

7.1 Collection Medium. 0.1 M hydrochloric acid. Fill a 1000-ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated hydrochloric acid, mix, and bring volume to the 1000-ml mark.

7.2 Hydrazine, reagent grade.

7.3 Methanol, reagent grade.

7.4 p-Dimethylaminobenzaldehyde. Prepare a 2.5% solution of p-dimethylaminobenzaldehyde in methanol.

7.5 Glacial acetic acid.

7.6 1.2 M sodium hydroxide.

7.7 Hydrazine Standard Solution. Pipet 3 ml hydrazine into a 100-ml volumetric flask. Bring to volume with methanol.

8. Procedure

8.1 Cleaning of equipment. All glassware should be washed in concentrated nitric acid, rinsed with triple distilled water, and rinsed with methanol. A final rinse with triple distilled water is made.

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 Pipet 10 ml of the 0.1 M hydrochloric acid (Section 7.1) into each bubbler, and mark the liquid level.

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 the pump on 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 1.0 liter per minute or less. A sample size of 100 liters is recommended.

8.3.4 After sampling, the bubbler stem may be removed and cleaned. If necessary, bring the volume of each sample to the 10-ml mark with 0.1 M hydrochloric acid. Wash the stem with approximately 1 ml of 0.1 M hydrochloric acid, 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 With each batch of ten samples, submit one bubbler from the same lot of bubblers which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.8 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 air samples.

8.4 Analysis of Samples

8.4.1 The sample in each bubbler is analyzed separately. The total volume of the solution should be 11 ml.*

8.4.2 Add 1 ml 1.2 M sodium hydroxide to the solution in the bubbler.

8.4.3 Immediately add 10 ml of 2.5% p-dimethylaminobenzaldehyde. Mix the solution and allow to stand for 30 minutes.

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*If the final volume of the solution is greater than 11 ml, an appropriate calculation adjustment must be made. If the volume is less than 11 ml, make it up to 11 ml with 0.1 M hydrochloric acid.

8.4.4 Transfer the resulting solution to a 25-ml volumetric flask.

8.4.5 Rinse the bubbler with approximately 1 ml of glacial acetic acid, adding rinse to the volumetric flask. Bring the solution to the 25-ml mark with the glacial acetic acid.

8.4.6 Mix the resulting orange solution, and pipet out a 1-ml aliquot of the solution into another clean 25-ml volumetric flask. Bring to volume with glacial acetic acid.

8.4.7 Adjust the baseline of the spectrophotometer to zero with distilled water in both cells.

8.4.8 Read at 480 nm in the spectrophotometer against a blank prepared in the same fashion as the samples.

9. Calibration and Standards

9.1 Pipet 11 ml of 0.1 M hydrochloric acid into each of six 25-ml volumetric flasks.

9.2 Carefully pipet 2, 4, 6, 8, and 10 microliters of the standard solution into the flasks (Section 7.7). Process one flask as a blank.

9.3 Add 1 ml 1.2 M sodium hydroxide to the flask.

9.4 Immediately add 10 ml of 2.5% p-dimethylaminobenzaldehyde and allow to stand for 30 minutes.

9.5 After 30 minutes, bring the volume in the flask to the 25-ml mark with glacial acetic acid.

9.6 Mix the resulting orange solution, and pipet out a 1-ml aliquot of the solution into another clean 25-ml volumetric flask. Bring to volume with glacial acetic acid.

9.7 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.

9.8 With the wavelength set at 480 nm, read the blank in the sample cell and then read the samples in the same cell or similar cells.

9.9 Construct a calibration curve by plotting absorbance against micrograms of hydrazine in the solution.

10. Calculations

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

10.2 Determine from the calibration curve (Section 9.9) the microgram of hydrazine present in each sample.

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m (mg/cu m = μg/liter).

$$\text{mg/cu m} = \frac{\mu\text{g (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

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 Dambrauskas, Thomas and Cornish, Herbert, "A Modified Spectrophotometric Method for the Determination of Hydrazine," Industrial Hygiene Journal, 23 (1962) 151.

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

Analyte:	Hydrogen Chloride	Method No.:	S246
Matrix:	Air	Range:	3.5-14 mg/cu m
OSHA Standard:	5 ppm (7 mg/cu m) - Ceiling	Precision ($\overline{CV}_T$):	0.064
Procedure:	Bubbler collection in 0.5 M sodium acetate, ion specific electrode	Validation Date:	1/30/76

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 sodium acetate solution.

   1.2 The resulting solution is diluted to 25 ml with distilled water.

   1.3 The diluted samples are analyzed using a chloride ion specific electrode.

2. Range and Sensitivity

   2.1 This method was validated over the range of 3.5-14 mg/cu m at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 15-liter sample. The probable useful range of this method is 1-20 mg/cu m for 15-liter samples.

   2.2 The upper limit of the range of the method is dependent on the capacity 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 chloride was determined to be 0.981, standard deviation of 0.005 (essentially 1.00), when sampled for 15 minutes at 0.94 liter per minute from a test atmosphere containing 70 mg/cu m. Therefore, no correction for collection efficiency is necessary.

3. Interferences

   3.1 This method is not specific for hydrogen chloride since any chloride ion which is trapped in the bubbler will be measured and give a positive interference.

3.2 Sulfide ion must be absent because it poisons the chloride ion electrode. Touch a drop of the sample to a piece of lead acetate paper to check for sulfide ion.

If sulfide is present, it is removed by addition of a small amount of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck a drop of the sample with lead acetate paper. Avoid a large excess of cadmium carbonate and long contact time with the solution. Filter the sample through a small plug of glass wool and proceed with the analysis.

3.3 Other common interfering ions are bromide ion, iodide ion, and cyanide ion. For interference-free operation, the chloride ion level must be at least 3×10^2 times the bromide ion level, 2×10^6 the iodide ion level, and 5×10^6 the cyanide ion level.

3.4 Sufficiently high concentrations of species which form extremely stable complexes with silver ion (such as ammonia and thiosulfate) will also interfere and will result in reading of higher chloride ion activity than actually exists. For less than a 1% error, the maximum ratio of ammonia to chloride concentration should be 0.12 and the maximum ratio of thiosulfate ion to chloride ion concentration should be 0.01.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.5-14 mg/cu m was 0.064. This value corresponds to a standard deviation of 0.45 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 0.981 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 2.7% 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 Section 10.4.

5. Advantages and Disadvantages of the Method

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

5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur which would invalidate the sample. If more than 5% of the sample volume is lost, the sample should be discarded.

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 15 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 Pipets: 1, 2, 3, 5, and 10 ml.

6.3 Orion Model 94-17A chloride specific ion electrode, or equivalent.

6.4 Reference electrode, Orion 90-02 double junction, or equivalent.

6.5 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.

6.6 Polyethylene beakers, 50-ml capacity. Premark the beakers by pipetting 25 ml of distilled water into each beaker and mark the liquid level. Pregraduated polyethylene beakers may be used. However, they should be checked as described above. Discard the water and dry the beakers.

6.7 Magnetic stirrer and stirring bars for 50-ml beakers.

6.8 Polyethylene containers. These containers should be used to store diluted sodium chloride standards and also for shipping of the samples.

6.9 100-ml volumetric flasks.

7. Reagents

All chemicals must be ACS reagent grade or equivalent.

7.1 Doubly distilled water.

7.2 Collection Medium: 0.5 M sodium acetate solution. Dissolve 82 g of sodium acetate in doubly distilled water and dilute to 2 liters.

7.3 Sodium chloride, for preparation of standards.

7.4 Standard Chloride Solution.

7.4.1 Dissolve 0.584 g of sodium chloride in double distilled water and dilute to 1 liter for 10^{-2} M (Cl^-) or 354 µg Cl^-/ml. Adjust the pH to 5 with glacial acetic acid. This solution is stable for about two months. The following more dilute standards should be prepared fresh weekly and kept in polyethylene containers.

7.4.2 Dilute 10 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 10^{-3} M (Cl^-) or 35.4 µg Cl^-/ml.

7.4.3 Dilute 5 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 5×10^{-4} M (Cl^-) or 17.7 µg Cl^-/ml.

7.4.4 Dilute 3 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 3×10^{-4} M (Cl^-) or 10.6 µg Cl^-/ml.

7.4.5 Dilute 2 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 2×10^{-4} M (Cl^-) or 7.1 µg Cl^-/ml.

7.4.6 Dilute 1 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 10^{-4} M (Cl^-) or 3.5 µg Cl^-/ml.

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 7.2) into the midget bubbler, using a graduated cylinder to measure the volume.

8.3.2 Connect the bubbler (via the splashover 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 15 minutes. The flow rate should be known with an accuracy of ± 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 remove the bubbler stem and transfer the contents of the bubbler to a polyethylene container. Rinse the bubbler and bubbler stem with 3-5 ml of collection medium, adding the rinse to the polyethylene container. Seal the polyethylene container with the associated caps just 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 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 polyethylene container is analyzed separately.

8.4.2 Quantitatively transfer the contents of each polyethylene container to a 50-ml polyethylene beaker which has been pre-marked at 25 ml. Rinse the polyethylene container with 2-3 ml of distilled water and add rinse to the beaker. Adjust the pH to 5 with acetic acid and check the pH with pH paper. Dilute each sample to 25 ml with distilled water and stir the samples with a magnetic stirrer.

8.4.3 Lower the chloride 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 a series of chloride standard solutions in the pre-marked 50-ml beakers by diluting 10 ml of each of the chloride standards prepared in Section 7.4.2-7.4.6, to a volume of 25 ml with double distilled water, starting with the most dilute standard. Place the chloride ion electrode and the double reference electrode in the stirred solution. Record the resultant millivolt readings to the nearest 0.5 millivolt.

9.2 Plot the millivolt readings vs. the chloride ion concentrations of the standards on semi-log paper. The chloride ion concentration in µg/25 ml is plotted on the logarithmic axis.

10. Calculations

10.1 Read the weight in µg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, because the standard curve is based on µg/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.

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

where:

µg sample = µg found in sample container
µg blank = µg found in blank container

10.3 Calculate the µg of hydrogen chloride by multiplying the µg chloride ion found (Section 10.2) by 1.028, which is the conversion factor to convert µg chloride ion to µg hydrogen chloride.

10.4 The concentration of the analyte in air sampled can be expressed in mg/cu m (mg/cu m = µg/liter).

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

10.5 Another method of expressing concentration is ppm.

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

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 "Analytical Method for Chloride in Air," Health Laboratory Science, Vol. 12, No. 3, (July 1975), 253-258.

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

Carbon Disulfide

Analyte:	Carbon Disulfide	Method No.:	S248
Matrix:	Air	Range:	14.7-58.8 ppm
OSHA Standard:	Ceiling - 30 ppm Peak - 100 ppm 8-hr. TWA - 20 ppm	Precision ($\overline{CV}_T$):	0.059
Procedure:	Adsorption on charcoal, desorption with benzene, GC	Validation Date:	1/30/76

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 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 for standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 14.7-58.8 ppm at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 6-liter sample. Under the conditions of sample size (6 liters) the probable useful range of this method is 5-90 ppm. 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 carbon disulfide and other substances in the air. The first section of the charcoal tube was found to hold 6.0 mg of carbon disulfide when a test atmosphere

containing 188 mg/cu m of carbon disulfide in air was sampled at 0.196 liter per minute for 162 minutes; breakthrough was observed at this time, i.e. 0.056 mg of carbon disulfide had broken through the front section of the charcoal tube during this time period. (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. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, carbon disulfide vapors may not be trapped efficiently. Experiments showed that there was increasing loss of carbon disulfide with an increase in relative humidity. In order to correct this problem, it is necessary to use a dessicant to remove the moisture (See Section 6.3).

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

3.3 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 14.7-58.8 ppm was 0.059. This value corresponds to a 1.8 ppm standard deviation at the ceiling 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 ceiling OSHA standard level using the overall sampling and analytical method were 0.7% 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 Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 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 two 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 Drying tubes: glass tube with both ends open, 7 cm long with a 6-mm O.D. and a 4-mm I.D. To add the dessicant into the tube, a plug of silylated glass wool is placed into one end of the tube, and the tube is filled with 270 mg of granular anhydrous sodium sulfate. Another plug of silylated glass wool is placed over the sodium sulfate, and the tube is capped at both ends.

6.4 Gas chromatograph equipped with a flame photometric detector, with a sulfur filter. The GC should be equipped with a vent as described in Section 8.4.4.

6.5 Column (6-ft X 1/4-in O.D. glass) packed with 5% OV-17 on 80/100 mesh Gas Chrom Q.

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

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

6.8 Pipets: 10-ml delivery pipets.

6.9 Volumetric flasks: 25-ml or convenient sizes for preparing standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Benzene, reagent grade.

7.3 Purified oxygen.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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, and dried.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube and a drying 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). Uncap both ends of the drying tube and connect this tube in series to the front section of the charcoal tube with 20 mm of Teflon tubing.

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearer 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 At the ceiling OSHA standard concentration, a sample size of 6 liters is recommended. Sample for 30 minutes at a flow rate of 0.20 liter per minute.

8.3.5 At the 8-hour time weighted average OSHA standard, a sample size of 12 liters is recommended. Sample at a flow rate of 0.20 liter per minute.

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 drying tube should remain connected to the charcoal tube during shipping. Cap the open end of the drying tube with a plastic cap. 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 With each batch of ten samples submit one charcoal tube and one drying tube from the same lot of tubes which were used for sample collection and which are subjected to exactly the same handling as the samples except that no air is drawn through it. Label this 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.

8.3.11 It has been found that carbon disulfide tends to migrate within the charcoal tube from the front section to the backup section when held at ambient temperatures for prolonged periods of time. This migration can effectively be retarded by storing the samples at refrigerator temperatures. The tubes appear to be unaffected by short storage at elevated temperatures or by shipping under reduced pressures. It is recommended that the samples be refrigerated if sample analysis cannot be performed within one week.

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 25-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, 10 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.

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

1. 20 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to detector
3. 35 ml/min air flow to detector
4. 20 ml/min oxygen gas flow to detector
5. 150°C injector temperature
6. 145°C detector temperature
7. 30°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column. To avoid exposing the detector to benzene the venting valve should be opened at 2-3 minutes after sample injection to elute the benzene and closed after the benzene is eluted.

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 64-mm 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 a benzene solution of carbon disulfide containing 0.14 mg/microliter 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 6-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the ceiling OSHA 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 10 ml of benzene with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of the 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/10 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/10 ml versus $(\text{peak area})^2$. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the flame photometric detector 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/10 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.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

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.

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

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 McCammon, C., Quinn, P., and Kupel, R., "A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide," Amer. Ind. Hyg. Assoc. J., 36, 618, August 1975.

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.

Carbon Dioxide

Analyte:	Carbon Dioxide	Method No.:	S249
Matrix:	Air	Range:	2270-10000 ppm
OSHA Standard:	5000 ppm (9000 mg/cu m)	Precision ($\overline{CV}_T$):	0.014
Procedure:	Collection in gas sampling bag, GC with thermal conductivity detector	Validation Date:	10/29/76

1. Principle of the Method

   1.1 A known volume of air is collected in a five-layer gas sampling bag by means of a low flow rate personal sampling pump capable of filling a bag.

   1.2 The carbon dioxide content of the samples is determined by gas chromatography using a thermal conductivity detector.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2270-9990 ppm at an atmospheric temperature of 20.5°C and atmospheric pressure of 757 mm Hg using a 3.5 liter sample volume. The working range of the method is estimated to be 500-15000 ppm, under the experimental conditions cited.

   2.2 The upper limit of the range of the method and the absolute sensitivity have not been established.

3. Interferences

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

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2270-9990 ppm was 0.014. This value corresponds to a 69-ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.5% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

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 samples in bags are analyzed by means of a quick instrumental method.

5.2. One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling and shipping.

6. Apparatus

6.1 Personal Sampling Pump. A personal sampling pump capable of filling a bag at approximately 0.05 liter per minute is required. This pump should be calibrated to within ±5%.

6.2 Gas Sampling Bag. 5-liter capacity; only the five-layer sampling bags manufactured by Calibrated Instruments, Inc. (731 Saw Mill Road, Ardsley, New York 10502) were found to be satisfactory for sample collection and storage for at least 7 days. The bag is fitted with a metal valve and hose bib. For the preparation of calibration standards in the laboratory, 5-liter Saran or Tedlar bags could be used.

6.3 Gas Chromatograph. The unit must be equipped with a thermal conductivity detector and a 5-milliliter gas sampling loop or equivalent. A portable unit with no column temperature control is adequate.

6.4 Column. (5-ft x 1/4-in stainless steel) packed with 80/100 mesh Porapak QS.

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

6.6 Gas-tight syringes. 10-ml and other convenient sizes for making standards.

6.7 Calibrated Rotameters. convenient sizes for making standards.

7. Reagents

7.1 Carbon dioxide, 99% or higher purity.

7.2 Nitrogen, purified.

7.3 Helium, purified.

7.4 Air, filtered compressed.

8. Procedure

8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the closure mechanism and bleeding out the air sample. The use of a vacuum pump is recommended although this procedure can be carried out by manually flattening the bags. The bags are then flushed with carbon dioxide-free air and evacuated. This procedure is repeated at least twice.

Bags may be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Observe for any discernable leaks and any volume changes or slackening of the bag, preferably over at least a one-hour period.

8.2 Calibration of Personal Pumps. Each personal pump should be calibrated to minimize errors associated with uncertainties in the sample volume collected. Although sample volume is not actually used in this determination, the pump should be calibrated to avoid over filling the bags; i.e., a maximum sampling time can be determined based on flow rate and sample volume which is approximately equal to 80% volume of bag.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, attach a small piece of Tygon or plastic tubing to the hose bib of the five-layer gas sampling bag.

8.3.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump.

8.3.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required.

8.3.4 A sample size of 3-4 liters is recommended. Sample at a flow rate of 0.05 liters per minute or less, but not less than 0.01 liters per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

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

8.3.6 The gas sampling bag should be labeled appropriately and sealed tightly.

8.3.7 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of getting punctured during shipping.

8.4 Analysis of Samples

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

1. 100 ml/min (25 psig) helium carrier gas flow
2. Ambient injector temperature
3. 70°C manifold temperature (detector)
4. Ambient column temperature

A retention time of approximately 2 minutes is to be expected for the analyte under these conditions and at ambient temperatures of 20-25°C using the column recommended in Section 6.4. The carbon dioxide elutes after oxygen and nitrogen.

8.4.2 GC Analysis. The gas sampling bag is attached to the sample loop of the GC unit via a short piece of tubing. Open the closure valve of the gas sampling bag and fill the 5-ml sample loop by gently squeezing the sample bag. To allow the sample in the loop to attain atmospheric pressure, release the pressure applied to the sample bag just prior to turning the sample loop valve to inject the sample onto the column.

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

9. Calibration and Standards

9.1 Completely evacuate a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Introduce 1.0 liter of filtered air via a septum into the bag; this can be done using a calibrated rotameter. Then add a known volume of carbon dioxide gas through a septum and add more air to a total accurately known volume of

between 3-4 liters. It is necessary to know accurately the volume of carbon dioxide added and the total volume of air to determine concentration in ppm. The concentration in ppm is equal to the volume of carbon dioxide divided by the sum of the volume of carbon dioxide and the volume of air.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in ppm versus peak area. Corrections for the unknown carbon dioxide concentration in the filtered air must be made if necessary. The carbon dioxide correction factor can be determined by filling an evacuated bag with 3-4 liters of the filtered air used for preparing the calibration standards. This "blank" air is analyzed under the same conditions as the calibration standards and the samples. The "blank" area thus determined is subtracted from the peak area of each calibration standard. A calibration curve is established by plotting concentration in ppm versus corrected peak area.

Note: Calibration standards should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in detector response.

10. Calculations

10.1 Read the concentration in ppm, corresponding to each peak area from standard curve.

10.2 Another method of expressing concentration is mg/cu m (corrected to standard conditions of 25°C and 760 mm Hg).

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

where:

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

11. References

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

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

Cyanide (as CN)

Analyte:	Cyanide	Method No.:	S250
Matrix:	Air	Range:	2.6-9.7 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.103
Procedure:	Collection with filter and impinger, Extraction with 0.1N NaOH, ion specific electrode	Validation Date:	1/30/76

1. Principle of the Method

1.1 Atmospheric samples are collected by drawing a known volume of air through a cellulose membrane filter and impinger (connected in series) containing 0.1N sodium hydroxide.

1.2 The sample-containing filters are extracted with 0.1N sodium hydroxide.

1.3 The filters and impingers are analyzed separately by direct potentiometry using an ion specific electrode.

1.4 The millivolt reading is used as a measure of cyanide concentration based on a calibration curve generated by measurement of standard solutions.

1.5 The samples must be carefully interspersed between calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.62-9.68 mg/cu m at an atmospheric temperature and pressure of 24°C and 763 mm Hg, using a 90-liter sample. Under the conditions of sample size (90 liters), the linear working range of the method is estimated to be 0.5-15 mg/cu m.

2.2 The lower limit of detection for cyanide is noted as 0.1 µg/ml.

3. Interferences

3.1 Gaseous hydrogen cyanide present in the air is an interference.

3.2 Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if found to be present in the sample. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

3.3 Sulfide is removed by the addition of a small amount (spatula tip) of powdered cadmium carbonate to the pH 11-13 sample. Swirl to disperse the solid and recheck the liquid by again touching a drop to a piece of lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution.

3.4 When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool contained in an eye dropper and proceed with the analysis.

3.5 It should also be noted that the cyanide electrode will malfunction if other ions like chloride, iodide and bromide, which form insoluble silver salts are present in sufficient quantity. Several metal ions are also known to complex with cyanide, such as cadmium, zinc, silver, nickel, cuprous, iron, and mercury. Consult the instruction manual for a list of these ions and also the proper procedure to use when such ions are believed to be present.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2.62-9.68 mg/cu m was 0.101. This value corresponds to a 0.5 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 A collection efficiency of 100% was determined for dry particulate cyanide on the cellulose membrane filter and a collection efficiency of 98% was determined for HCN in 0.1N NaOH; thus, no bias was introduced in the sample collection step based on collection efficiency. Likewise, data on a limited number of analytical filter samples give an average recovery of 97%. In the absence of a significant amount of "free" HCN in the environment being sampled, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

Advantages are the simplicity, specificity, and speed of the method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal samples for the determination of cyanide content consists of the following components.

6.1.1 A filter unit which consists of the filter media (Section 6.2) and 37-mm, 3-piece cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter and impinger in the line.

6.1.4 Thermometer

6.1.5 Manometer

6.1.6 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Polyethylene scintillation vials with screw caps, 20 ml.

6.4 Orion 94-06 Cyanide ion specific electrode or equivalent.

6.5 Orion 90-20-00 double junction reference electrode or equivalent.

6.6 A pH meter with readout capacity in increments of 0.1 millivolt.

6.7 Magnetic Stirrer and Stirring Bars.

6.8 Jars for extraction of filters: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

6.9 Pipets, 10 ml and other convenient sizes.

6.10 Volumetric flasks, 25 ml and other assorted sizes.

6.11 Associated laboratory glassware.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 Double distilled water

7.2 Potassium Cyanide

7.3 Sodium Hydroxide 0.1N. Dissolve 2.0 g NaOH in double distilled water and dilute to 500 ml.

7.4 Cyanide Standards

7.4.1 Cyanide Standard Stock solution, 200 µg/ml. Dissolve 0.50 g KCN in 0.1N NaOH and dilute to 1000 ml with additional 0.1N NaOH.

7.4.2 Working standards. Prepare at least 6 working standards to cover the concentration range of interest by proper dilution of the stock standard to a total volume of 25 ml. Use 0.1N NaOH for all dilutions. Prepare these calibration standards fresh daily.

7.5 Lead Acetate Paper

7.6 Cadmium Carbonate

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Calibration of Personal Pump. Personal sampling pump should be calibrated using integrating volume meter (6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 To collect cyanide salts, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1) connected in series to a midget impinger containing 10 ml of 0.1N NaOH.

8.3.2 The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter.

8.3.3 A short piece of flexible tubing is used to connect the filter holder to the impinger. A similar piece of flexible tubing, loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation, is used to connect the impinger to the sampling pump. The impinger must be maintained in a vertical position during the sampling. Clip the cassette to the worker's lapel.

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

8.3.5 Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and

pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation, Position the middle of the rotameter ball of the personal sampling pump to the 1.5 liter per minute calibration mark as accurately as possible. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

8.3.6 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. The sample should be taken at a flow rate of 1.5 liters per minute for 60 minutes (90 liters).

8.3.7 After sampling disconnect the filter holder cassettes from the impingers and firmly seal the cassettes with the plugs in both the inlet and outlet.

8.3.8 The sample impingers are then handled and shipped separately from the filters. The impinger stems can be removed and cleaned as follows. Tap the stem gently against the inside wall of the impinger bottom to recover as much of the sampling solution as possible and quantitatively transfer the total contents of the impinger bottom into a 20-ml polyethylene scintillation vial with screw cap. Wash the impinger stem with 2 ml of 0.1N NaOH and add washing into the polyethylene vial. Close cap tightly and secure with plastic tape around edges to avoid sample loss during transit.

8.3.9 Care should be taken to minimize spillage or loss by evaporation at all times.

8.3.10 Carefully record sample identity of both filters and impingers and all relevant sample data.

8.3.11 Blank. With each batch of 10 samples, submit one filter and one impinger solution which is subjected to exactly the same handling as for the samples except that no air is drawn through them. Label these as blanks. Submit one blank filter and one blank impinger solution for every ten samples.

8.4 Analysis of Samples

8.4.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 2 oz. ointment jar.

8.4.2 Pipet 25 ml of 0.1N NaOH into the jar. Cap and allow to stand for at least 30 minutes with occasional shaking. Tests indicate that this period is adequate for complete extraction of the cyanide from the filter. Analyze these filter samples within 2 hours after extraction.

8.4.3 The impinger sample solutions contained in the polyethylene vials are also made up to a 25-ml volume.

8.4.4 Potentiometric Measurements.

1. The samples are analyzed by immersing the cyanide ion electrode and reference electrode in the sample solutions and recording the millivolt reading. Both the samples and standards should be stirred while the readings are being taken. The reading should be taken after the meter has stabilized. Follow instrument manufacturer's instruction manual for proper operation and measurement procedures.

2. To obtain the most reliable results, the samples should be carefully interspersed with standards of similar response.

8.4.5 Appropriate filter blanks and impinger blanks must be analyzed by the same procedure used for the samples.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method for particulate cyanide, it is necessary to determine the recovery of the analyte. The analyte recovery should be determined in duplicate for at least one concentration which corresponds to a weighable amount. If the recovery of the analyte is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A weighed amount of the analyte, preferably equivalent to the concentration expected in the sample, is added to a representative cellulose membrane filter. The analyte is then recovered from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm$5%.

For this validation study, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level has been used for the recovery studies. Six filters were spiked with weighed amounts of potassium cyanide equivalent to the CN present at 2X OSHA standard level. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All

filters were then analyzed as described in Section 8.4. The average recovery value obtained was found to be 97%.

The recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 Prepare a series of working standards containing 40-1000 micrograms of cyanide in 25 ml of 0.1N sodium hydroxide. These standards should be prepared fresh each time. Refer to Section 7.4. It is convenient to express concentration of standards in terms of µg per 25 ml, because samples are in this volume of solvent.

9.2 The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice will minimize the effect of observed fluctuations or variations in millivolt readings during any given day.

9.3 On semilog paper, plot the millivolt readings vs. cyanide ion concentrations of the standards. The cyanide ion concentration in µg/25 ml is plotted on the log axis.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the millivolt response of the sample by using the appropriate response factor or calibration factor for the sample.

10.2 Separately calculate the amount of particulate cyanide found on the filter and the cyanide (HCN) found in the impinger.

10.3 Corrections for the blank must be made for each sample filter and impinger.

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

where:

µg sample = µg found in sample filter or sample impinger
µg blank = µg found in blank filter or blank impinger

10.4 Divide the total weight of CN from filter by the recovery to obtain the corrected µg/sample.

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

10.5 Report the particulate cyanide found and the HCN found as separate values because the OSHA standards for these two species are different. Note that the HCN found may be due to free HCN as well as HCN formed from moisture interaction with the particulate CN during sampling.

10.6 If HCN is known to be absent in the environment being sampled, then the sum of the CN found on the filter and the impinger solution gives a total measure of particulate cyanide.

10.7 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.8 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Instruction Manual for cyanide ion specific electrode.

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

Dimethyl Acetamide

Analyte:	Dimethyl Acetamide	Method No.:	S254
Matrix:	Air	Range:	18.17-105.6 mg/cu m
OSHA Standard:	10 ppm (35 mg/cu m)-skin	Precision ($\overline{CV}_T$):	0.067
Procedure:	Adsorption on silica gel, desorption with methanol, GC	Validation Date:	1/30/76

1. Principle of the Method

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 methanol.

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 18.17-105.6 mg/cu m at an atmospheric temperature and pressure of 24°C and 760 mm Hg, using a 45-liter sample. Under the conditions of sample size (45 liters) the probable useful range of this method is 10-105 mg/cu m. 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 22.2 mg of analyte when a test atmosphere containing

105.6 mg/cu m of analyte in air was sampled at 0.876 liter per minute for 240 minutes; at that time the concentration of dimethyl acetamide in the effluent was less than 5% of that in the influent. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 18.17-105.6 mg/cu m was 0.067. This value corresponds to a 2.3 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.

1.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which a desorption efficiency 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. 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 11.1)

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 (6-ft long X 1/4-in. O.D. stainless steel) packed with 20% UCON 50LB 550X on Chromosorb P 60/80 treated with 20% KOH.

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

6.10 Ultrasonic bath.

7. Reagents

7.1 Methanol, reagent grade.

7.2 Dimethyl Acetamide, reagent grade.

7.3 Acetone, 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 nearer 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 $\pm$ 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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

8.3.9 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 methanol 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. 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. 240°C injector temperature
5. 320°C manifold temperature (detector)
6. 160°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 64 mm , 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 an acetone solution of dimethyl acetamide containing 472 μg/μl is injected directly into the silica gel with a microliter syringe. Cap the silica gel tube

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 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 methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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 methanol, because samples are desorbed in this amount of methanol. The density of the analyte is used to calculate milligrams from 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 methanol and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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. Reference

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

Analyte:	Dimethyl Formamide	Method No.:	S255
Matrix:	Air	Range:	10.61-61.1 mg/cu m
OSHA Standard:	10 ppm (30 mg/cu m) - skin	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on silica gel, desorption with methanol, GC	Validation Date:	1/30/76

1. Principle of the Method

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 methanol.

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 10.61-61.1 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 45-liter sample. Under the conditions of sample size (45 liters) the probable useful range of this method is 10-90 mg/cu m. 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 dimethyl formamide and other substances in the air. The first section of the silica gel tube was found to hold 15 mg of dimethyl formamide when a test atmosphere containing 119.5 mg/cu m of dimethyl formamide in air was sampled at 0.859 liter per minute for 146 minutes; breakthrough was

observed at this time, i.e., the concentration of dimethyl formamide in the effluent was 5% of that in the influent. (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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 10.61-61.1 mg/cu m was 0.056. This value corresponds to a 1.7 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 was determined for the collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which a desorption efficiency 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. 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ± 5% at the recommended flow rate. (Reference 11.1)

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 (6-ft long X 1/4-in. O.D. stainless steel) packed with 20% UCON 50LB 550X on Chromosorb P 60/80 treated with 20% KOH.

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

6.10 Ultrasonic bath.

7. Reagents

7.1 Methanol, reagent grade.

7.2 Dimethyl Formamide, reagent grade.

7.3 Acetone, 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 nearer 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 $\pm$ 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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

8.3.9 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 methanol 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. 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. 240°C injector temperature
5. 320°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel

and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 64 mm , 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 an acetone solution of dimethyl formamide containing 380 μg/μl is injected directly into the silica gel with a microliter syringe. Cap the silica gel tube 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 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 methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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 methanol, because samples are desorbed in this amount of methanol. The density of the analyte is used to calculate milligrams from 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 methanol and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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. Reference

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

Carbon Black

Analyte:	Carbon Black	Method No.:	S262
Matrix:	Air	Range:	1.86-7.7 mg/cu m
OSHA Standard:	3.5 mg/cu m	Precision ($\overline{CV}_T$):	0.056
Procedure:	Filter collection, Gravimetric analysis	Validation Date:	1/30/76

1. Principle of the Method

1.1 A known volume of air is drawn through tared polyvinyl chloride filters to collect carbon black.

1.2 The sample-containing filters are removed from the cassette and dried over a desiccant to constant weight using a suitable microbalance.

2. Range and Sensitivity

2.1 This method for carbon black was validated over the range of 1.86-7.7 mg/cu m at an atmospheric temperature and pressure range of 18-25°C and 749-761 mm Hg, using a 200-liter sample. Under the conditions of sample size (200 liters), the working range of the method is estimated to be 1.5-10 mg/cu m or a 0.3-2 mg total weight of material collected on the filter.

It was also validated for a 100-liter sample over the range of 7.8-27.7 mg/cu m at atmospheric temperature and pressure conditions as above.

2.2 The method may be extended to higher sample concentrations by collecting a smaller sample volume; this will prevent collection of too much sample particulate so as to cause sample loss due to flaking.

3. Interferences

3.1 The presence of any other particulate material in the air being sampled will be a positive interference since this is a gravimetric method.

3.2 Information on any other particulate materials present should be solicited. If the concentration of other particulates is known, then the carbon black concentration can be determined by difference. If other particulate matter is known to be present and

its concentration cannot be determined, then this method will not provide an accurate measure of the carbon black concentration.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 1.86-7.7 mg/cu m was 0.056. This value corresponds to a 0.20 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 98.7% was determined for the collection medium at the 2X level; thus, no bias was introduced in the sample collection step. Likewise, no significant bias in the analytical method is expected other than normal gravimetric errors. CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The analysis is simple but the method is non-specific and subject to interference due to presence of other particulates in the air being sampled.

6. Apparatus

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of carbon black has the following components:

6.1.1 The filter unit, consisting of the filter media, stainless steel support screen (Section 6.2) and 37-mm three-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Polyvinyl chloride membrane filter; 37-mm diameter, 2.0-micrometer pore size.

6.3 PetriSlide (Millipore) or plastic Petri dish as filter holder for storage and weighing.

6.4 Desiccator

6.5 Microbalance capable of weighing to 10 micrograms. Particular care must be given to proper zeroing of the balance. The same balance should be used for weighing filters before and after sample collection.

7. Reagents

Drierite or any other suitable desiccant.

8. Procedure

8.1 Preparation of Filters - All filters must be dried and weighed prior to use.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect carbon black, a personal sampler pump is used to pull air through a polyvinyl chloride membrane filter (Section 6.2). The filter holder is held together by tape or a shrinkable band. If the filter holder is not tightened snugly, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.7 liters per minute. After sampling, replace small plugs to seal filter cassettes.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 If the outer surface of the cassette filter holder is heavily coated with dust, carefully swab the outer surface with a moist paper towel before opening the cassette so as to minimize sample contamination. Discard paper towel.

8.3.2 Open the cassette filter holder and carefully remove the polyvinyl chloride membrane filter from the holder and stainless steel screen with the aid of Millipore filter tweezers. Transfer filter to a PetriSlide.

8.3.3 Dry the filter to constant weight in a desiccator containing a desiccant. This takes about 12 hours.

8.3.4 Weigh the filter in a microbalance.

8.3.5 If other particulate matter is suspected to be present, appropriate analyses should be made to determine its composition (if necessary) and quantity. This value should be subtracted from the total particulate weight.

9. Calibration and Standards

This portion is not applicable. The only standardization required is that the microbalance be properly zeroed for all weighings and preferably the same microbalance should be used for weighing filters before and after sample collection.

10. Calculations

10.1 Record the tare weight, in µg, of the dry filter before sampling.

10.2 Record the weight, in µg, of the dried, sample-containing filter.

10.3 The difference between these two weights represents the µg sample.

10.4 Corrections for the blank must be made for each sample. (If found to be necessary, corrections should also be made for other other particulate matter.)

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.5 Convert volume of air sampled to standard conditions of 25°C and and 760 mm Hg.

$$Vs = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where

Vs = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = barometric pressure in mm Hg
T = ambient air temperature in degrees centigrade

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{µg found (Section 10.4)}}{\text{Vs}}$$

11. Reference

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

Ethyl Silicate

Analyte:	Ethyl silicate	Method No.:	S264
Matrix:	Air	Range:	377-1620 mg/cu m
OSHA Standard:	100 ppm (850 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on XAD-2 resin, desorption with carbon disulfide, GC	Validation Date:	2/27/76

1. Principle of the Method

1.1 A known volume of air is drawn through a tube containing XAD-2 resin to adsorb the ethyl silicate present.

1.2 The XAD-2 resin 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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 377-1620 mg/cu m at an atmospheric temperature and pressure of 2[illegible]°C and 771 mm Hg, using a 9-liter sample. Under the conditions of sample size (9 liters) the probable useful range of this method is 85-1700 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 15-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used. When higher concentrations of ethyl silicate are expected, a smaller sample volume should be collected.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the XAD-2 resin tube. This capacity varies with the concentrations of analyte and other substances in the air. Breakthrough studies indicated that the first section of the XAD-2 resin tube was found to hold 24 mg of analyte when a test atmosphere containing 1640 mg/cu m of analyte in air was sampled at 0.80 liter per minute for 18 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent.

The collection efficiency of ethyl silicate on the XAD-2 resin tube may be dependent on sample flow rate. A separate study gave a collection efficiency of 98% for 9-liter samples collected at 0.067 liter per minute for concentration levels at 2 times the OSHA standard.

The resin tube consists of two sections of XAD-2 resin separated by a section of silylated glass wool. (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 The adsorptive capacity of XAD-2 resin is not severely affected by water vapor. Breakthrough volume will not be substantially affected by high relative humidity. Note, however, that although ethyl silicate is not soluble in water, it is slowly decomposed by water (Merck Index).

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 as 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 377-1620 mg/cu m was 0.056. This value corresponds to a 48 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 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 7.1% 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.

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

5. Advantages and Disadvantages of the Method

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

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the resin 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 ±5% at the recommended flow rate. (Reference 11.2)

6.2 Resin tubes: glass tube with both ends flame-sealed, 7 cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin, prepared as described in Section 7.7. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the outlet end of the tube and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. 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% OV-101 stationary phase on 100/120 mesh Supelcoport.

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

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

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

6.8 Pipets: 2.0 ml, delivery type.

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

6.10 Glass rods, 3 mm, or cylindrical wooden medical applicators.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Ethyl silicate, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 Filtered compressed air

7.7 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a standard Soxhlet extractor. Larger batches may be prepared by using a Giant extractor. Overnight (24 hr) extractions are then performed successively with water, methyl alcohol, diethyl ether and, finally, n-pentane. Distilled-in-glass solvents are used in all cases. Resin has been prepared successfully in this manner using charges of about 700 g of resin and 1.5 liters of each solvent. The resin is dried by maintaining it under vacuum (1-10 torr) and mild heat for about 24 hours.

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 XAD-2 resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, 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 XAD-2 resin is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The XAD-2 resin tube should be placed in a vertical direction during sampling to minimize channeling through the resin.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the coated XAD-2 resin tube.

8.3.5 A maximum sample size of 9 liters is recommended. Sample at a rate of 0.05 liter per minute only. 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 XAD-2 resin tubes should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube for every 10 samples 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 XAD-2 resin tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of samples

1. In preparation for analysis, each sample tube is scored with a file in front of the backup and the front section and broken open at both ends to give a wider tube opening for easier transfer of the resin bed.

2. Remove the glass wool plug next to the backup section (exit end) and discard. Transfer the resin from the backup section into a 5-ml vial.

3. Then remove the glass wool plug at the front end of the 100 mg section and transfer to a separate 5-ml vial. Carefully transfer the resin into the same

5-ml vial. If the resin particles tend to hang on to the inner walls of the glass tube instead of flowing freely, use the remaining glass wool plug to push out the rest of the resin particles. A short piece of 3-mm glass rod or a wooden medical applicator can be used for this purpose.

4. In the event that difficulties are encountered in the transfer operation due to electrostatic charges which make the resin particles cling to the glass walls, it is suggested that the tubes be flushed with a gentle stream of air or nitrogen presaturated with water for 5-10 seconds.

8.4.2 Desorption of Samples. Prior to analysis, 2.0 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. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 ml of carbon disulfide containing a known amount of the chosen internal standard. If an automatic sample injector is used, transfer at least a 1-ml aliquot of the desorbed sample solution to the automatic sample injector vial.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 100°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 technique.

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 may vary from one laboratory to another and also from one batch of XAD-2 resin 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 XAD-2 resin is used.

8.5.2 Procedure for determining desorption efficiency. An amount of the XAD-2 resin equivalent to that present 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 resin must be from the same batch as that used in obtaining the samples and can be obtained from unused XAD-2 resin tubes. The open end is capped with Parafilm. A known amount of ethyl silicate is injected directly into the resin with a microliter syringe, and the tube is capped with more Parafilm. Alternatively, a 5-ml vial capped with a Teflon-faced septum may be used in place of the glass tube.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 9-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the XAD-2 resin. 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

Two or three standards are prepared by injecting the same volume of compound into 2.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

The desorption efficiency is dependent on the amount of analyte collected on the resin. 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 per 2.0 ml of carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the ethyl silicate is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 2.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per 2.0 ml is plotted versus the ratio of the area of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID responses.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because

the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

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

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2 for the amount found in the front 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 At the recommended sampling rate of 0.05 liter per minute and a sample volume of 9.0 liters, no correction for collection efficiency is necessary. The collection efficiency was determined to be at least 98% under these conditions.

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

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

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

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

where:

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

11. References

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

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

Oil Mist, Mineral*

Analyte:	Oil Mist	Method No.:	S272
Matrix:	Air	Range:	2.5-11.7 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$:)	0.065
Procedure:	Filter collection. Extraction with chloroform, Fluorescence	Validation Date:	2/27/76

1. Principle of the Method

1.1 Air samples are collected using 37-mm cellulose ester membrane filters.

1.2 Oil mist is extracted from the filters with chloroform.

1.3 The chloroform solution is analyzed for oil content using fluorescence spectrophotometry.

2. Range and Sensitivity

2.1 This method was validated using a sample of machine cutting oil over the range of 2.5-11.7 mg/cu m at an atmospheric temperature and pressure of 22°C and 75' mm Hg using a 100-liter sample. Under the conditions of sample size (100 liters), the working range of the method is estimated to be 0.05-15 mg/cu m provided that the linear response range is not exceeded.

2.2 The method may be extended to higher concentrations by further dilution of the sample.

2.3 The fluorescence characteristics of various oils differ and therefore the sensitivity and linear range of the method will vary depending on the oil sample. Non-linearity can occur beyond a certain concentration range depending on the oil sample as a result of fluorescence quenching. Thus, it is important to establish the linear range of the oil in question by using the bulk sample as reference.

3. Interferences

3.1 Mineral oils (aromatic free) and paraffin oils will not be detected by this method.

*Not all mineral oils can be detected by fluorescence analysis.

3.2 Highly fluorescent compounds may interfere in this analysis.

3.3 Any specie or impurity which can cause quenching will be a negative interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2.5-11.7 mg/cu m was 0.065. This value corresponds to a 0.3 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 11.3.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method--the average recovery from the filters was 97.7%. 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 method is simple and fast. It is specific for the oil used in the calibration.

5.2 Some very light oils do not fluoresce sufficiently and cannot be analyzed using this method. In all cases a bulk sample of the oil in question must be provided for use in the preparation of standards for the analysis.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of oil mist has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - a calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$5%, at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Manometer

6.1.4 Thermometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Fluorescence spectrophotometer with both excitation and analyzer scanning capabilities in the range of 250-550 mμ.

6.4 1-cm cells for fluorescence spectrophotometer.

6.5 Jars for sample extraction; 2 oz. ointment jars, squat form with aluminum lined screw caps.

7. Reagents

7.1 Chloroform - Spectroquality, distilled in glass or equivalent.

7.2 Stock Solution, 100 mg/ml - Weigh 10.00 g of oil into a 100 ml volumetric flask and dissolve with chloroform to volume.

8. Procedure

8.1 Cleaning of Equipment:

8.1.1 Wash in detergent solution and follow with tap water and distilled water rinses.

8.1.2 Rinse thoroughly with acetone, then with portions of the distilled chloroform, and allow to dry.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect the analyte aerosol a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.2 Blank: With each batch of samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every 10 samples.

8.2.3 Shipping: The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.2.4 A bulk sample of the oil being used must be collected and sent to the laboratory for use as a standard

material in the analysis. To prevent contamination, the bulk should not be shipped in the same container as the samples.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to the extraction jar.

8.3.2 Pipet 10 ml of chloroform into the jar and tightly close the jar to minimize solvent evaporation.

8.3.3 Allow to stand for at least 30 minutes with occasional agitation. At this point the oil is in solution and the samples are ready for analysis.

8.3.4 Determine the proper excitation wavelength for the analysis using an oil solution containing 100 µg/ml. This solution is prepared by proper dilution of the stock solution with chloroform.

8.3.5 Transfer the sample and blank solutions to 1-cm cells and record a fluorescence spectrum for each solution using the previously determined excitation wavelength.

8.3.6 The peak-height of the largest fluorescent peak is used to measure the oil concentration from the calibration curve prepared from the bulk samples (Section 8.2.4).

8.3.7 When analyzing unknown samples, it is advisable to do a sequential sample dilution to check for "self-quenching" indicated by non-linear response.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within $\pm$5%.

For the validation study conducted to determine the precision and accuracy of the method, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The recovery values obtained were 97.7% and as such no correction factor has been used in the determination of the "true" values.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 Appropriate dilutions of the stock solution with chloroform are made to obtain working standards in the range of 1.0 µg/ml to 100 µg/ml.

9.2 The working standards are transferred to 1-cm cells and a fluorescence spectrum is obtained for each standard. A calibration curve is constructed by measuring the peak height of the largest fluorescent peak and plotting this value vs. concentration in µg/ml.

10. Calculations

10.1 Determine the concentration, in µg/ml, corresponding to the peak height of the largest fluorescent peak present in the sample by using the appropriate calibration or response factor determined from the response of the calibration standards. Multiply by the total volume and/or appropriate dilution factor to determine total sample weight in µg.

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

µg = µg sample - µg blank

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the determined weight by the recovery to obtain the corrected µg/sample

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = Volume of air in liters at 25°C and 760 mm Hg
V^s = Volume of air sampled
P = Pressure (mm Hg) of air sampled
T = Temperature (°C) of air sampled
760 = Standard pressure (mm Hg)
298 = Standard temperature (°K)

11. References

11.1 Roy, E.M., American Industrial Hygiene Journal, 31, 472 (1970).

11.2 Lippmann, M., et al, Arch. Environ. Health, 21, 591 (1970).

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

Carbaryl
(Sevin)

Analyte:	Carbaryl	Method No.:	S273
Matrix:	Air	Range:	1.96-13.43 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.057
Procedure:	Filter collection, colorimetric	Validation Date:	2/27/76

1. Principle of the Method (Reference 11.1)

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 Methanol that is 0.1 M in KOH is added to the filter to extract the analyte and hydrolyze it. An aliquot is then reacted with p-nitrobenzenediazonium fluoroborate to form a colored complex.

1.4 The absorption at 475 nm is used as a quantitative measure of carbaryl.

2. Range and Sensitivity

2.1 This method was validated over the range of 1.96-13.43 mg/cu m, at an atmospheric temperature and pressure of 24°C and 763 mm Hg. The probable range of the method is 0.1-18 mg/cu m based on the range of standards used to prepare the standard curve. For samples of higher concentration where the absorbance is greater than the limits of the standard curve, the samples may be diluted with methanolic potassium hydroxide (prior to removal of an aliquot to use for color development) to extend the upper limit of the range.

2.2 A concentration of 0.5 mg/cu m of carbaryl in a 90-liter air sample gives a 0.05 absorbance using a 1-cm cell.

3. Interferences

3.1 Phenols such as 1-naphthol will give a positive interference.

3.2 Any compound which absorbs at 475 nm, or which reacts under the conditions of analysis to form an absorbing species, is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.96-13.43 mg/cu m was 0.057. This value corresponds to a 0.28 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 was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 The sampling 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 2-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.2) at the recommended flow rate.

6.1.3 Manometer.

6.1.4 Thermometer.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter must be free of organic binders. The filter is held in the two-piece filter holder supported by a backup pad.

6.3 Spectrophotometer. This instrument should be capable of measuring the developed color at 475 nm.

6.4 Matched glass cells or cuvettes, 1-cm path length.

6.5 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal. These bottles are also used to contain the solution during analysis.

6.6 Tweezers.

6.7 A 10-ml glass syringe with Luer-Lok tip. A stainless steel Luer-Lok fitted filter holder is attached to the syringe, and holds 13-mm Teflon filters.

6.8 Assorted laboratory glassware--pipets and volumetric flasks of appropriate capacities.

7. Reagents

7.1 Carbaryl, analytical grade.

7.2 0.1 M potassium hydroxide in absolute methanol.

7.3 p-Nitrobenzenediazonium fluoroborate. Dissolve 25 mg in 5 ml absolute methanol. Add 20 ml of glacial acetic acid to this solution. Prepare fresh daily.

7.4 Glacial acetic acid.

7.5 Carbaryl Standard Solution. Dissolve 460 mg carbaryl in 10 ml methylene chloride.

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, and dried.

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 two-piece filter cassette holder and close firmly. The filter is held in place by a 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 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 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 glass fiber filter should be removed from the cassette filter holder within 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 for 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 Each filter is analyzed separately.

8.4.2 Add 20 ml of 0.1 M methanolic potassium hydroxide to the screw top jar containing the filter.

8.4.3 Place the jar on a mechanical wrist-action shaker for 5 minutes.

8.4.4 Transfer 2 ml of the solution to a clean screw top jar.

8.4.5 Add 17 ml glacial acetic acid and immediately cover the jar with a Teflon lined screw cap. Mix by swirling.

8.4.6 Add 1 ml p-nitrobenzenediazonium fluoroborate solution. The color will develop in 3-5 minutes. The sample should be analyzed in 20 minutes.

8.4.7 The solution will contain glass fibers from the filter. Use the 10-ml syringe fitter with a filter holder containing the Teflon filter to transfer the solution from the jar to the 1-cm cell (Section 6.7). The solution is poured into the barrel of the syringe, and forced through the filter into the cell by moving the plunger down the barrel.

8.4.8 Adjust the baseline of the spectrophotometer to zero with distilled water in both cells.

8.4.9 Read the absorbance of the sample at 475 nm against a blank prepared in the same fashion as the samples.

9. Calibration and Standards

9.1 Pipet 20 ml of 0.1 M methanolic potassium hydroxide into each of six 25-ml volumetric flasks.

9.2 Carefully pipet 3, 8, 15, 25, and 35 microliters of the standard solution into the flasks (Section 7.5). Process one flask as a blank.

9.3 After 5 minutes, pipet 2 ml of each solution into a clean 25-ml volumetric flask.

9.4 Add 17 ml of glacial acetic acid and mix.

9.5 Add 1 ml of p-nitrobenzenediazonium fluoroborate solution. Mix.

9.6 Allow the solution to react for 20 minutes.

9.7 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.

9.8 With the wavelength set at 475 nm, read the absorbance of the sample against the absorbance of the blank.

9.9 Construct a calibration curve by plotting absorbance against micrograms of carbaryl in the standard.

10. Calculations

10.1 Determine from the calibration curve (Section 9.9) the micrograms of carbaryl present in each sample.

10.2 The concentration of the analyte in the air sampled can be expressed in mg/cu m (mg/cu m = μg/liter).

$$\text{mg/cu m} = \frac{\mu\text{g (Section 10.1)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Official Methods of Analysis, A.O.A.C., 1970, p. 493.

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

DDT

2,2-bis (p-chlorophenyl)-1,1,1-trichloroethane

Analyte:	DDT	Method No.:	S274
Matrix:	Air	Range:	0.49-2.60 mg/cu m
OSHA Standard:	1.0 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.062
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date:	2/27/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with iso-octane. An aliquot of the extract is analyzed by gas chromatography.

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 0.494-2.60 mg/cu m at an atmospheric temperature and pressure of 26°C and 760 mm Hg, using a 90-liter sample. The probable useful range of this method is 0.10-0.30 mg/cu m for 90-liter samples.

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

3. Interferences

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

3.2 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.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.494-2.60 mg/cu m was 0.061. This value corresponds to a standard deviation of 0.06 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 collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method, since analytical method recovery corrections were 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

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

6. Apparatus

6.1 The sampling 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 two-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Manometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.2 Glass fiber filter, similar to Gelman Type AE with a 37-mm diameter. The filter must be free of organic binders. The filter is held in the two-piece filter holder supported by a backup pad. The glass fiber filter should be at least 99.7% efficient against particles as small as 0.3 microns.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.5 Column (4-ft long X 1/2-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.8 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.9 Pipets of convenient sizes.

6.10 Tweezers.

7. Reagents

7.1 DDT, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Benzene, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

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, and dried.

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 two-piece filter cassette holder and close firmly. The filter is held in place by a 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 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm 5\%$.

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 glass fiber filter should be removed from the cassette filter holder within 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 for 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 Each sample is analyzed separately.

8.4.2 Pipet 15 ml of iso-octane into each screw cap bottle.

8.4.3 Swirl the contents in each bottle occasionally for one hour.

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

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

1. 115 ml/min nitrogen carrier gas flow
2. 35 ml/min hydrogen gas flow to furnace
3. 790°C furnace temperature
4. 225°C transfer temperature
5. 260°C vent temperature
6. 190°C column temperature

8.4.6 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 25-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 1.0 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 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.5), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the three levels (0.5X, 1X, and 2X the OSHA standard) using a stock solution of 225 mg of DDT in 2 ml of benzene and diluting to 10 ml with iso-octane. Three sets of six filters are spiked with appropriate volumes of the stock solution to correspond to the amount of DDT which would be collected in a 90-liter sample at the 0.5X, 1X, and 2X the OSHA standard level. Allow the filters to dry and place each filter in a cassette filter holder and allow to stand overnight. The filters are extracted and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

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

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, are prepared from the above stock solution. Dilute standards are prepared by diluting measured volumes of stock solution to known volumes with iso-octane. The standards are analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

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

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

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

where:

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

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

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

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

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

11. Reference

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

Aldrin

Analyte:	Aldrin	Method No.:	S275
Matrix:	Air	Range:	0.15-0.50 mg/cu m
OSHA Standard:	0.25 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.092
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date:	2/27/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane to collect the analyte.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial.

1.3 An aliquot from the scintillation vial is analyzed by gas chromatography.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 0.149-0.495 mg/cu m at an atmospheric temperature and pressure of 25°C and 760 mm Hg, using a 165-liter sample. The probable lower limit of the useful range of this method is 0.025 mg/cu m.

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

3. Interferences

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

3.2 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.

4. Precision and Accuracy

4.1 The Coefficienct of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.149-0.495 mg/cu m was 0.092. This value corresponds to a standard deviation of 0.023 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 collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which no analytical method recovery correction was necessary. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

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

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

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

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of aldrin has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder connected in series with a midget bubbler (Section 6.3). Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter is held in the two-piece cassette filter holder. A backup pad should not be used. The filter must be free of organic binders and should be at least 99.7% efficient against particles as small as 0.3 micron.

6.3 A glass midget bubbler containing 15 ml of the collection medium (Section 7.2).

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

6.5 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.6 Column (4-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.10 Pipets of convenient sizes.

6.11 Tweezers.

7. Reagents

7.1 Aldrin, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Benzene, reagent grade.

7.4 Prepurified hydrogen.

7.5 Purified nitrogen.

8. Procedure

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

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

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of the collection medium (Section 7.2) into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked at least every 15 minutes. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the bubbler at the end of sampling should be 12 ml or less.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.

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

8.3.5 A sample size of 180 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of ±5%.

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

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

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

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

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

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

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

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Prior to injection of the sample into the GC, swirl the contents in the vial for five minutes.

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

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

1. 160 ml/min nitrogen carrier gas flow
2. 140 ml/min hydrogen gas flow to furnace
3. 750°C furnace temperature
4. 225°C transfer temperature
5. 205°C vent temperature
6. 190°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 25-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 1.0 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 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 20 seconds was adequate to elute the solvent. 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 in Section 9.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, is prepared from a stock solution of aldrin in benzene/iso-octane solution (1:5) containing 11.275 mg/ml. Dilute standards are prepared by diluting measured volumes of stock solution to known volumes with iso-octane. The standards are analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

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

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

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

where:

mg sample = mg found in sample filter and bubbler
mg blank = mg found in blank filter and bubbler

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.2) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

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

p-Dichlorobenzene

Analyte:	p-Dichlorobenzene	Method No.: S281
Matrix:	Air	Range: 183.2-777 mg/cu m
OSHA Standard:	75 ppm (450 mg/cu m)	Precision ($\overline{CV}_T$): 0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 3/26/76

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 183.2-777 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 75-1350 mg/cu m. 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 p-dichlorobenzene and other substances in the air. The first section of the charcoal tube was found to hold at least 8.4 mg of p-dichlorobenzene when a test atmosphere containing 777 mg/cu m of p-dichlorobenzene in air was sampled at 0.045 liter per minute for 240 minutes. (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. Interferences

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

3.3 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 183.2-777 mg/cu m was 0.052. This value corresponds to a 23 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 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which a desorption efficiency 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. 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ±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. 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: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 p-Dichlorobenzene, reagent grade.

7.3 Acetone, reagent grade.

7.4 p-Dichlorobenzene standard solution. Weigh out 3.50 g of p-dichlorobenzene into a small beaker and add approximately 7 ml of acetone. Warm the solution gently to dissolve the p-dichlorobenzene. Quantitatively rinse the resulting solution into a 10-ml volumetric flask and bring to volume with acetone.

7.5 Purified nitrogen.

7.6 Prepurified 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 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 nearer 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 3 liters is recommended. Sample at a flow rate of 0.05 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 With each batch of ten samples submit one tube from the same lot of tubes 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.

8.3.9 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. 225°C injector temperature

5. 275°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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 64 mm, 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 an acetone solution of p-dichlorobenzene

(Section 7.4) 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 3-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

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

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. 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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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.

Analyte:	Dieldrin	Method No.: S283
Matrix:	Air	Range: 0.12-0.59 mg/cu m
OSHA Standard:	0.25 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.086
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date: 3/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with iso-octane. An aliquot of the extract is analyzed by gas chromatography.

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 0.122-0.587 mg/cu m at an atmospheric temperature and pressure of 22°C and 759 mm Hg, using a 170-liter sample. The probable useful range of this method is 0.25-0.75 mg/cu m for 170-liter samples.

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

3. Interferences

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.122-0.587 mg/cu m was 0.086. This value corresponds to a standard deviation of 0.02 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 collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no significant bias in the sampling and analytical method, so no analytical method recovery corrections were 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

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

6. Apparatus

6.1 The sampling 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 two-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Manometer

6.1.4 Thermometer

6.1.5 Stopwatch

6.2 Glass fiber filter, similar to Gelman Type AE with a 37-mm diameter. The filter must be free of organic binders. The filter is held in the two-piece filter holder supported by a backup pad. The glass fiber filter should be at least 99.7% efficient against particles as small as 0.3 micron.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.5 Column (4-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.8 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.9 Pipets of convenient sizes.

6.10 Tweezers.

7. Reagents

7.1 Dieldrin, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Benzene, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

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, and dried.

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 two-piece filter cassette holder and close firmly. The filter is held in place by a 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 glass fiber filter should be removed from the cassette filter holder within 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 for 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 Each sample is analyzed separately.

8.4.2 Pipet 15 ml of iso-octane into each screw cap bottle.

8.4.3 Swirl the contents in each bottle occasionally for one hour.

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

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

1. 160 ml/min nitrogen carrier gas flow
2. 140 ml/min hydrogen gas flow to furnace
3. 770°C furnace temperature
4. 225°C transfer temperature
5. 260°C vent temperature
6. 190°C column temperature

8.4.6 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 25-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 1.0 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 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.5), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. 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. Crystalline dieldrin is weighed and made up to volume in a volumetric flask. Stock solutions are prepared in 1:5 mixtures by volume of benzene/iso-octane. These solutions will keep indefinitely if the flask is well stoppered. Dilute standards are prepared by diluting measured volumes of stock solutions to known volumes with iso-octane. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

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

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

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

where:

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

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

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

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

EPN

O-Ethyl-O-p-nitrophenyl phenylphosphonothiolate

Analyte:	EPN	Method No.: S285
Matrix:	Air	Range: 0.295-1.156 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.059
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date: 4/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with iso-octane. An aliquot of the extract is analyzed by gas chromatography.

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 0.295-1.156 mg/cu m at an atmospheric temperature and pressure of 20°C and 759 mm Hg, using a 115-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m for 115-liter samples.

2.2 The method is capable of measuring higher concentrations than those tested. If higher concentrations are sampled, the samples can be diluted with iso-octane prior to analysis.

3. Interferences

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

3.2 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.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.295-1.156 mg/cu m was 0.059. This value corresponds to a standard deviation of 0.030 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 collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 The sampling 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 2-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Manometer.

6.1.4 Thermometer.

6.2 Glass fiber filter, Type AE with a 37-mm diameter. The filter must be free of organic binders. The filter is held in the two-piece filter holder supported by a backup pad.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph with a flame photometric detector with a phosphorous filter.

6.5 Column (6-ft long X 1/4-in O.D. glass) packed with 3% OV-1 on 100/120 mesh Gas Chrom Q.

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

6.7 Tweezers.

6.8 Microliter syringes: 10-microliter.

6.9 Volumetric flasks: Convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes for preparing standard solutions and 15-ml pipets for measuring the collection medium.

7. Reagents

7.1 EPN, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Purified oxygen.

7.6 Filtered compressed air.

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, and dried.

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 two-piece filter cassette holder and close firmly. The filter is held in place by a 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 120 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of ±5%.

8.3.5 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 glass fiber filter should be removed from the cassette filter holder within 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 for 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 Each sample is analyzed separately.

8.4.2 Pipet 15 ml of iso-octane into each screw cap bottle.

8.4.3 Swirl the contents in each bottle occasionally during a period of one hour.

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

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

1. 60 ml/min nitrogen carrier gas flow
2. 125 ml/min hydrogen gas flow to detector
3. 20 ml/min oxygen gas flow to detector
4. 35 ml/min air flow to detector
5. 205°C column temperature
6. 215°C detector temperature
7. 215°C injector temperature

8.4.6 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column. Since a 5-microliter aliquot is likely to cause the flame to blow out, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions (Section 8.4.5), it was found that 30 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. 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/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the flame photometric detector response.

10. Calculations

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

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

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

where:

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

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

$$mg/cu\ m = \frac{mg\ (Section\ 10.2) \times 1000\ (liter/cu\ m)}{Air\ Volume\ Sampled\ (liter)}$$

11. Reference

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

Ethylene Oxide

Analyte:	Ethylene Oxide	Method No.:	S286
Matrix:	Air	Range:	41-176 mg/cu m
OSHA Standard:	50 ppm (90 mg/cu m)	Precision ($\overline{CV}_T$):	0.103
Procedure:	Adsorption on charcoal, descrption with carbon disulfide, GC	Validation Date:	3/27/76

1. Principle of the Method

1.1 A known volume of air is drawn through a large charcoal tube to trap the organic vapors present. The sampling tube consists of two separate tubes--a front adsorbing tube and a backup tube. This sampling arrangement is necessary to prevent sample migration effects upon storage.

1.2 The charcoal in each tube is transferred to a 5-ml, screw-capped 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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 41-176 mg/cu m at an atmospheric temperature and pressure of 26°C and 761 mm Hg, using a 5-liter sample. Under the conditions of recommended sample size (5 liters) the probable useful range of this method is 20-270 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1.4-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the front charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The front adsorbing charcoal tube was found to hold 2.1 mg of analyte when a test atmosphere containing 280 mg/cu m of analyte in air was sampled at 0.19 liter per minute for 40 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube series consists of two separate large tubes; the first tube contains 40 mg of charcoal and the second tube used as the backup tube contains 200 mg of charcoal. The charcoal is held in place by glass wool plugs at the tube ends. 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 operation conditions described in this method is an interference. Retention time data on a single column cannot be considered as 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 41-176 mg/cu m is 0.103. This value corresponds to an 9.3 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 0.9% 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.

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 charcoal tube exceeds 25% of that found on the front tube, 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 ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: The sampling tube series consists of two separate large charcoal tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with an 8-mm O.D. and a 6-mm I.D. Each tube contains the appropriate amount of 20/40 mesh activated coconut charcoal. The front tube contains 400 mg of charcoal; the backup tube 200 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

The sampling tubes can be prepared by modifying commercially available large charcoal tubes as follows. To prepare the front tube, break off exit end of a large tube and using pointed tweezers remove glass wool plug and the backup charcoal section; push in snugly remaining plug and charcoal to minimize channeling. To prepare the backup tube, similarly break off inlet end of a second large tube and remove retaining plug and the front charcoal section; again push together remaining plug and charcoal. The front tube is connected to the backup tube with a minimal piece of tygon or rubber tubing. This sampling tube scheme is necessary to minimize any sample migration effects upon storage.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with Porapak QS.

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

6.6 Five-milliliter sample containers with Teflon-lined screw caps, such as the 5-ml vials distributed by SKC, Inc., Pittsburgh, Pa.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

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

6.8 Pipets: 2.0 ml, graduated or delivery.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Ethylene oxide, 99.5%. Available as a liquid or a gas.

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 sampling tube series in the line assembled as noted in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube (3 mm). Prepare and assemble as described in Section 6.2. Connect the front 400-mg tube to the 200-mg backup tube with a short piece of tubing.

8.3.2 The tube containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube series 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 tubes.

8.3.5 A sample size of 5 liters is recommended. Sample at a rate of 0.05 liter per minute. 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 front charcoal tube should be separated from the backup tube immediately after sampling. Both tubes must be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 One set of tubes prepared as described in Section 6.2 should be handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through these tubes. These tubes should be labeled as blanks.

8.3.9 Capped charcoal 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 and broken open. The glass wool is removed and discarded. The charcoal in the front tube is transferred to a 5-ml sample container with Teflon-lined screw cap. Similarly, the charcoal in the backup tube is transferred to another container. These two charcoal tubes are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 2.0 ml of carbon disulfide is pipetted into each sample container. Cap the vials tightly immediately after the addition of carbon disulfide. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, carefully transfer portions of the desorbed sample solution to the automatic sample injector vials and cap

tightly. For the internal standard method, desorb using 2.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 155°C injector temperature
5. 200°C manifold temperature (detector)
6. 150°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 blowback 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 technique.

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 front tube (400 mg) is measured into a 10-cm long, 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 a concentrated solution of the analyte in carbon disulfide* is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. Alternatively, the 5-ml tubes or vials used for desorption may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 5-liter sample at the selected level. The tubes are 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 ethylene oxide solution in carbon disulfide into 2.0 ml of carbon disulfide with the same syringe used in the preparation of the spiked samples. These are analyzed with the samples.

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

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

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.

*This solution of ethylene oxide in carbon disulfide can be prepared by bubbling ethylene oxide gas into carbon disulfide in a fritted glass bubbler. The ethylene oxide concentration of the solution is determined by comparison with gas standards. The solution can also be prepared by using ethylene oxide liquid. Note that the syringe used must be cooled; otherwise the liquid ethylene oxide will evaporate very rapidly. This solution must be calibrated as above.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 2.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The calibrated solution of ethylene oxide in carbon disulfide as described in Section 8.5.2 can be used to prepare calibration solutions. In the preparation of standard solutions, observe the necessary precautions noted as a footnote to Section 8.5.2. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 2.0 ml versus peak area.

Standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

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

where:

mg sample = mg found in front (400-mg) sample tube
mg blank = mg found in front (400-mg) blank tube

A similar procedure is followed for the backup tube.

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

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

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

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 100 (Liters/cu m)}}{\text{Air Volume Sampled (Liters)}}$$

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

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

where:

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

11. References

11.1 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.

Analyte:	Lindane*	Method No.:	S290
Matrix:	Air	Range:	0.28-1.66 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.086
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date:	3/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane to collect the analyte.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial.

1.3 An aliquot from the scintillation vial is analyzed by gas chromatography.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 0.278-1.662 mg/cu m at an atmospheric temperature and pressure of 24°C and 760 mm Hg, using a 90-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m.

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

*Gamma benzene hexachloride

3. Interferences

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

3.2 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.

4. Precision and Accuracy

4.1 The Coefficienct of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.278-1.662 mg/cu m was 0.086. This value corresponds to a standard deviation of 0.043 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 collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which no analytical method recovery correction was necessary. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

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

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

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

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of lindane has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder connected in series with a midget bubbler (Section 6.3). Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter is held in the two-piece cassette filter holder. A backup pad should not be used. The filter must be free of organic binders and should be at least 99.7% efficient against particles as small as 0.3 micron.

6.3 A glass midget bubbler containing 15 ml of the collection medium (Section 7.2).

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

6.5 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.6 Column (4-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: Convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes.

6.11 Tweezers.

7. Reagents

7.1 Lindane, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Benzene, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

8. Procedure

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

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

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of the collection medium (Section 7.2) into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked at least every 15 minutes. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the bubbler at the end of sampling should be 12 ml or less.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.

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

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

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

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

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

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

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

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

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

8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Prior to injection of the sample into the GC, swirl the contents in the vial for five minutes.

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

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

1. 150 ml/min nitrogen carrier gas flow
2. 140 ml/min hydrogen gas flow to furnace
3. 770°C furnace temperature
4. 225°C transfer temperature
5. 260°C vent temperature
6. 160°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent with the syringe needle, one should employ the solvent flush injection technique. The 25-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 1.0 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 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 20 seconds was adequate to elute the solvent. 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 in Section 9.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest is prepared from a stock solution of lindane in benzene/iso-octane solution (1:5) containing 11.25 mg/ml. Dilute standards are prepared by diluting measured volumes of stock solution to known volumes with iso-octane. The standards are analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

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

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

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

where:

mg sample = mg found in sample filter and bubbler
mg blank = mg found in blank filter and bubbler

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.2) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

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

Naphthalene

Analyte:	Naphthalene	Method No.:	S292
Matrix:	Air	Range:	19.3-83 mg/cu m
OSHA Standard:	10 ppm (50 mg/cu m)	Precision ($\overline{CV}_1$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/26/76

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 19.3-83 mg/cu m at an atmospheric temperature and pressure of 21°C and 774 mm Hg, using a 200-liter sample. Under the conditions of sample size (200 liters) the probable useful range of this method is 15-150 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 30-mg sample. 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 analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 19.4 mg of analyte when a test atmosphere containing 81.1 mg/cu m of analyte in air was sampled at 1.0 liter per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

(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 as 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 19.3-83 mg/cu m was 0.055. This value corresponds to a 2.8 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 0.5% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can

be eliminated by altering chromatographic conditions. The 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 ±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% OV-101 stationary phase on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

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

7. Reagents.

7.1 Chromatographic quality carbon disulfide.

7.2 Naphthalene, reagent grade.

7.3 Undecane, or other suitable internal standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 of 200 liters is recommended. Sample at a rate 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. Submit one blank for every 10 samples.

8.3.9 Capped charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 125°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5, 1, and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 200-liter sample at the selected level. A concentrated solution of naphthalene in carbon disulfide may be used for spiking. The tubes are 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 the naphthalene solution used into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

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 per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

11.1 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.

Nicotine

Analyte:	Nicotine	**Method No.:**	S293
Matrix:	Air	**Range:**	0.30-1.20 mg/cu m
OSHA Standard:	0.5 mg/cu m	**Precision ($\overline{CV}_T$):**	0.066
Procedure:	Adsorption on XAD-2 resin, desorption with ethyl acetate GC/alkali FID	**Validation Date:**	3/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a tube containing XAD-2 resin to adsorb the nicotine present.

1.2 The XAD-2 resin in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with ethyl acetate.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph with an alkali-flame ionization detector.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 0.295-1.195 mg/cu m at an atmospheric temperature and pressure of 23°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 0.05-1.5 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.15 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used. When higher concentrations of nicotine are expected, a smaller sample volume should be collected.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the XAD-2 resin tube. This capacity varies with the concentrations of analyte and other substances in the air. Breakthrough studies indicated that the first section of the XAD-2 resin tube was found to hold at least 0.2 mg of analyte when a test atmosphere containing 1.2 mg/cu m of analyte in air was sampled at 1.1 liter per minute for 180 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

The resin tube consists of two sections of XAD-2 resin separated by a section of silylated glass wool. (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 The adsorptive capacity of XAD-2 resin is not severely affected by water vapor. Breakthrough volume will not be substantially affected by high relative humidity.

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 as 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 0.295-1.195 mg/cu m was 0.066. This value corresponds to a 0.03 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 100% was determined for the collection medium at the 2X OSHA standard test level for a sample size of 100 liters; thus, no bias was introduced in the sample collection step. Any bias due to desorption efficiency has also been controlled by correcting the "found" values for the appropriate DE factor which ranged from 0.90 to 0.98 over the concentration range equal to 0.5 to 2X OSHA standard for a 100-liter sample. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can

be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the resin 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 ±5% at the recommended flow rate. (Reference 11.2)

6.2 Resin tubes: glass tube with both ends flame-sealed, 7 cm long with 6 mm O.D. and 4 mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin, prepared as described in Section 7.7. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the outlet end of the tube and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. 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 an alkali-flame ionization detector.

6.4 Column (6-ft x 1/4 in. glass, 2 mm I.D.) packed with 3% OV-101 stationary phase on 100/120 mesh Supelcoport.

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

6.6 Sample containers, 2 ml or 5 ml, with glass stoppers or Teflon-lined caps.

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

6.8 Pipets: 100 ml, delivery type.

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

6.10 Glass rods, 3 mm, or cylindrical wooden medical applicators.

7. Reagents

7.1 Chromatographic quality ethyl acetate

7.2 Nicotine, reagent grade

7.3 Diphenylamine, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

7.7 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a standard Soxhlet extractor. Larger batches may be prepared by using a Giant extractor. Overnight (24 hr) extractions are then performed successively with water, methyl alcohol, diethyl ether and, finally, n-pentane. Distilled-in-glass solvents are used in all cases. Resin has been prepared successfully in this manner using charges of about 700 g of resin and 1.5 liters of each solvent. The resin is dried by maintaining it under vacuum (1-10 torr) and mild heat for about 24 hours.

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 XAD-2 resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, 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 XAD-2 resin is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The XAD-2 resin tube should be placed in a vertical direction during sampling to minimize channeling through the resin.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the coated XAD-2 resin tube.

8.3.5 A sample size of 100 liters is recommended. Sample at a rate 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 XAD-2 resin tubes should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube for every 10 samples 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 labelled as a blank.

8.3.9 Capped XAD-2 resin tubes should be packed tightly and padded before they are shipped, to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of samples

1. In preparation for analysis, each sample tube is scored with a file in front of the backup and the front section and broken open at both ends to give a wider tube opening for easier transfer of the resin bed.

2. Remove the glass wool plug next to the backup section (exit end) and discard. Transfer the resin from the backup section into a 5-ml vial.

3. Then remove the glass wool plug at the front end of the 100 mg section and transfer to a separate 5-ml vial. Carefully transfer the resin into the same 5-ml vial. If the resin particles tend to hang on to the inner walls of the glass tube instead of flowing freely, use the remaining glass wool plug to push out the rest of the resin particles. A short piece of 3 mm glass rod or a wooden medical applicator can be used for this purpose.

4. In the event that difficulties are encountered in the transfer operation due to electrostatic charges which make the resin particles cling to the glass

walls, it is suggested that the tubes be flushed with a gentle stream of air presaturated with water for 5-10 seconds.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of ethyl acetate is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of ethyl acetate containing a known amount of the chosen internal standard. If an automatic sample injector is used, the desorbption can be done in the automatic sample injector vials.

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

1. 25 ml/min (50 psig) Helium carrier gas flow
2. 35 ml/min (40 psig) Hydrogen gas flow to detector
3. 200 ml/min (60 psig) air flow to detector
4. 235°C injector temperature
5. 260°C manifold temperature (detector)
6. 165°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. Two 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 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1-2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. 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 technique.

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 may vary from one laboratory to another and also from one batch of XAD-2 resin 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 XAD-2 resin is used.

8.5.2 Procedure for determining desorption efficiency. An amount of the XAD-2 resin equivalent to that present 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 resin must be from the same batch as that used in obtaining the samples and can be obtained from unused XAD-2 resin tubes. The open end is capped with Parafilm. A known amount of a solution of nicotine in ethyl acetate is injected directly into the resin with a microliter syringe, and the tube is capped with more Parafilm. Alternatively a 5-ml vial or the 2-ml automatic sample injector vial capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5, 1 and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 100-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the XAD-2 resin. 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 ethyl acetate with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of ethyl acetate containing a known amount of the internal standard.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the resin. 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 per 1.0 ml of ethyl acetate, because samples are desorbed in this amount of ethyl acetate. The density of the nicotine is used to convert µg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use ethyl acetate containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 75% of the concentration at 2X the standard. The analyte concentration in mg per 1.0 ml is plotted versus the area ratio of the analyte to that of the internal standard. The compound used as internal standard must not be adsorbed by XAD-2 resin. Check for adsorption losses by adding 1.0 ml of the internal standard stock solution to 100 mg of XAD-2 resin and allow to stand for at least 30 minutes. If there are no adsorption losses, the area response obtained from a 2-µl aliquot of this blend should equal the area response obtained from an equal aliquot of the original stock solution of internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in alkali-FID responses.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml ethyl acetate and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

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

A similar procedure is followed for the backup section.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

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

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

Parathion

Analyte:	Parathion	Method No.:	S295
Matrix:	Air	Range:	0.0726-0.2643 mg/cu m
OSHA Standard:	0.11 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.078
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date:	3/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with iso-octane. An aliquot of the extract is analyzed by gas chromatography.

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 0.0726-0.2643 mg/cu m at an atmospheric temperature and pressure of 20°C and 762 mm Hg, using a 115-liter sample. The probable useful range of this method is 0.011-.33 mg/cu m for 115-liter samples.

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

3. Interferences

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

3.2 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.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.0726-0.2643 mg/cu m was 0.078. This value corresponds to a standard deviation of 0.0085 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 collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 The sampling 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 2-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Manometer.

6.1.4 Thermometer.

6.2 Glass fiber filter, Type AE with a 37-mm diameter. The filter must be free of organic binders. The filter is held in the two-piece filter holder supported by a backup pad.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph equipped with a flame photometric detector with a phosphorous filter.

6.5 Column (6-ft long x 1/4-in. O.D. glass) packed with 3% OV-1 on 100/120 mesh Gas Chrom Q.

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

6.7 Tweezers.

6.8 Microliter syringes: 10-microliter.

6.9 Volumetric flasks: Convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes for preparing standard solutions, and 15-ml pipets for measuring the collection medium.

7. Reagents

7.1 Parathion, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Purified oxygen.

7.6 Filtered compressed air.

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, and dried.

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 two-piece filter cassette holder and close firmly. The filter is held in place by a 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 120 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 glass fiber filter should be removed from the cassette filter holder within 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 for 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 Each sample is analyzed separately.

8.4.2 Pipet 15 ml of iso-octane into each screw cap bottle.

8.4.3 Swirl the contents in each bottle occasionally for one hour.

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

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

1. 60 ml/min nitrogen carrier gas flow
2. 135 ml/min hydrogen gas flow to detector
3. 20 ml/min oxygen gas flow to detector
4. 35 ml/min air flow to detector
5. 165°C column temperature
6. 200°C detector temperature
7. 215°C injector temperature

8.4.6 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, 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. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column. Since a 5-microliter aliquot is likely to cause the flame to blow out, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.5), it was found that 30 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. 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/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the flame photometric detector response.

10. Calculations

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

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

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

where:

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

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

$$mg/cu\ m = \frac{mg\ (Section\ 10.2) \times 1000\ (liter/cu\ m)}{Air\ Volume\ Sampled\ (liter)}$$

11. Reference

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

Thallium, Soluble Compounds as Tl

Analyte:	Thallium	**Method No.:**	S306
Matrix:	Air	**Range:**	0.034-0.15 mg/cu m
OSHA Standard:	0.1 mg/cu m	**Precision ($\overline{CV}_T$):**	0.060
Procedure:	Filter collection, Acid digestion, Atomic absorption	**Validation Date:**	4/23/76

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix and the sample solution is diluted to volume with water.

1.2 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. An electrodeless discharge lamp or hollow cathode lamp for thallium is used to provide a characteristic thallium line at 276.8 nm. The absorbance is proportional to the thallium concentration within a limited concentration range.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.034-0.15 mg/cu m at an atmospheric temperature and pressure of 22°C and 759 mm Hg, using a 540-liter sample. Under the conditions of sample size (540 liters), the working range of the method is estimated to be 0.02-0.25 mg/cu m.

2.2 The method may be extended to higher sample concentrations by further dilution of the sample solution.

3. Interferences

3.1 The method as described is for total thallium; therefore, the presence of insoluble thallium compounds will interfere, either as positive (like acid soluble thallium) or negative (like water soluble but acid insoluble) interference. Thus, it is necessary to obtain a bulk sample in order to test for solubility. An acid digestion route is recommended because studies using thallium sulfate, Tl_2SO_4 showed low recoveries from the filter when extraction with water was used (Reference 11.3).

3.2 There are no known spectral line interferences due to other elements in the thallium assay.

4. **Precision and Accuracy**

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.034-0.15 mg/cu m was 0.060. This value corresponds to a 0.006 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 11.3.

4.2 A collection efficiency of 99.1% was determined for the collection medium at the 2X level; thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method--the average recovery from the filters was 99.9%. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The analysis is both simple and specific for thallium but does not distinguish a priori between soluble and insoluble thallium compounds.

6. **Apparatus**

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Thallium electrodeless discharge lamp or thallium hollow cathode lamp: The electrodeless discharge lamp works linearly over the concentration range of 0.01 to 20 µg/ml as compared to a linear range of 0.03 to 20 µg/ml for the hollow cathode lamp.

6.3.2 Oxidant: compressed air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used

6.4 Glassware, borosilicate:

6.4.1 125 ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25 ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Double distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Aqueous standard stock solutions containing 1000 µg/ml of thallium (commercially available).

7.4 Thallium working standard solution, 20 µg/ml. Prepare by appropriate dilution of above solution. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect particulate thallium, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers. Transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process two more times using 2 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to dryness.

8.3.3 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.4 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.

8.3.5 Rinse each beaker at least twice with 5 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.6 Dilute all samples to 25 ml with distilled water.

8.3.7 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 276.8 nm. The absorbance is proportional to the analyte concentration in the sample and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample could be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.6 than is necessary to effect a quantitative transfer.

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

8.3.8 Appropriate filter blanks must be analyzed by the same procedure for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within $\pm$5%.

For the validation study, an amount of the analyte equivalent to that present in a 540-liter sample at the selected level was used for recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then ashed and analyzed as described in Section 8.3. The average recovery value obtained was found to be 99.9%.

The percent recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}} \times 100$$

8.5 **Determination of Solubility of Bulk Sample**

8.5.1 **Need for determination.** This step is necessary in order to support any data obtained from the sample analysis because the acid digestion procedure described is a general method for soluble thallium as well as insoluble thallium compounds which are acid soluble.

8.5.2 Procedure for determining solubility

1. Weigh 0.500 g of the bulk sample and dissolve in water. Dilute to 25 ml and analyze as described in Section 8.3.7. Compare with known standards to determine amount of soluble thallium. Make appropriate sample dilution if the absorbance reading obtained falls outside the linear range.

2. Weigh another 0.500 g of the bulk sample and treat with 2 ml of concentrated nitric acid and warm gently. Cool and dilute to 25 ml. Analyze as described in Section 8.3.7 and above.

3. The data obtained by these two procedures will indicate the presence or absence of soluble and insoluble thallium.

9. Calibration and Standards

9.1 From the 20 µg/ml working standard solution, prepare at least 6 working standards to cover the range from 10 to 200 µg/25 ml. Since the low concentration standards may deteriorate, the standard solutions should be made fresh each day.

9.2 Proceed as in Section 8.3.6 to 8.3.8.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

µg found = µg sample - µg blank

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V^s = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

Arsenic and Compounds (as As)

Analyte:	Arsenic	Method No.:	S309
Matrix:	Air	Range:	0.198-0.903 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.058
Procedure:	Filter collection, acid digestion, flameless atomic absorption	Validation Date:	9/26/75

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

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the arsenic (including arsenic compounds) is then solubilized in nitric acid.

   1.3 The solutions of samples and standards are pipetted into the graphite furnace of an atomic absorption spectrophotometer (AAS). An electrodeless discharge lamp for arsenic is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.198-0.903 mg/cu m using an 85-liter sample at an atmospheric temperature and pressure of 24.5°C and 743 mm Hg. Under the conditions of sample size (85 liters), the working range of the method is estimated to be 0.1-1.3 mg/cu m.

   2.2 The sensitivity of this method using the 100-ml final solution volume is 0.8 µg (0.008 µg/ml for a 1% absorption). The method may be expanded by adjusting the final volume.

3. Interferences

   There are no known interferences for the arsenic atomic absorption spectrophotometric assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.198-0.903 mg/cu m is 0.058. This value corresponds to a 0.029 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, 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 quick, instrumental method.

5.2 This method will measure particulate arsenic and its compounds that are trapped by the mixed cellulose ester filter. Volatile arsenic compounds will not be measured.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of arsenic content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

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

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region, a direct readout (or recorder output) proportional to absorbance units, a graphite furnace accessory and a background corrector accessory. The Perkin-Elmer 305B with the HGA 2000 graphite furnace and Deuterium Background Corrector is an example. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 193.7 nm wavelength.

6.3.1 Arsenic electrodeless discharge lamp.

6.3.2 High purity nitrogen.

6.3.3 Pressure reducing valve. A 2-gauge, 2-stage pressure reducing valve and appropriate hose connection are needed for the nitrogen supply tank.

6.3.4 A suitable method for measuring peak heights or areas.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.4.4 Eppendorf 25-µl pipettor with tips.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Arsenic trioxide, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 Dilute nitric acid (2 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water).

7.5 Perchloric acid, 60% solution.

7.6 40% sodium hydroxide.

7.7 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of arsenic.

8. Procedure

8.1 Cleaning of Equipment

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

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

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 **Wet Ashing.** Treat the sample in each beaker with 10 ml of concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of the beaker, and allow the solution to evaporate a small volume. Do not overheat.

8.4.3 Cool each beaker and dissolve residues in 5 ml dilute nitric acid.

8.4.4 Quantitatively transfer the clear solutions to a 100-ml volumetric flask.

8.4.5 Rinse each beaker at least twice with 5 ml portions of dilute nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 100 ml with dilute nitric acid.

8.4.6 Pipette 25 µl of the solutions into the graphite tube using an automatic pipettor (such as the Eppendorf pipettor) with disposable plastic tips.

The instrumental parameters for graphite furnace tube source power, background corrector and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying, charring and atomizing should be established in accord with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of arsenic during these steps.

To obtain reliable results, samples must be frequently alternated with standards which give responses close to those of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate and reinject a standard in duplicate, ... etc.

Note: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak heights or areas, it must be rejected and replaced because results so obtained are not reliable.

8.4.7 Record the absorbance at 193.7 nm. Peak heights are used for this measurement if the response is rapid and the bases of the peaks are short and reproducible. If the bases of the peaks are broadened by the presence of contaminants, the areas of the absorption peaks will give more accurate measurements. Area measurements may be made by the use of a planimeter or an electronic integrator.

8.4.8 When very low concentrations are found in the sample, the sample can be dried and redissolved to a smaller volume such as 25 or 50 ml and reinjected.

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

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery.

Six filters are spiked at each of three levels (0.5X, 1X, and 2X the OSHA standard). Appropriate amounts of arsenic trioxide are dissolved in 5 ml of 40% sodium hydroxide and diluted to 250 ml with distilled water to represent each of the three OSHA levels. Three sets of six filters are spiked with appropriate volumes of each standard solution for each of the three levels. This corresponds to the amount of arsenic collected in a 90-liter sample at the 0.5X, 1X and 2X levels, respectively. Allow the filters to dry and place each filter in a cassette filter holder, and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

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

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

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 15 to 80 µg/100 ml from the 1000 µg/ml stock arsenic standard solution. Make all standard solutions in dilute nitric acid and prepare fresh daily.

9.2 To determine the response, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbances during any given day.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbances versus the concentration of each standard in µg/100 ml.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/100 ml.

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

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

where:

µg sample = µg found in sample filter

µg blank = µg found in blank filter

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

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

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3)}}{\text{Air Volume Samples (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

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

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

Aniline

Analyte:	Aniline	Method No.: S310
Matrix:	Air	Range: 9.54-38.2 mg/cu m
OSHA Standard:	5 ppm (19 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.060
Procedure:	Adsorption on silica gel, desorption with 95% ethanol, GC	Validation Date: 7/4/75

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 9.54-38.2 mg/cu m at an atmospheric temperature and pressure of 22°C and 759 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 1.7 mg of analyte when a test atmosphere containing

38.2 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. At that time the concentration of analyte in the effluent was less than 5% of that in the influent. (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 interferring compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 9.54-38.2 mg/cu m was 0.060. This value corresponds to a 1.14 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 4.7% 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 Section 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 +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 Aniline, reagent grade.

7.3 Benzene, reagent grade.

7.4 n-Hexane, reagent grade.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

7.7 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 0.20 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 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 With each batch of ten samples, submit one tube from the same lot of tubes 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.

8.3.9 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. 245°C manifold temperature (detector)
6. 165°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 benzene-hexane solution of aniline containing 102.2 mg/ml is injected directly into the silica gel with a microliter syringe. The benzene-hexane solution of aniline was prepared by dissolving 1 ml of aniline in 2 ml of benzene in a 10-ml volumetric flask and bringing to volume with hexane. Cap the silica gel tube 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

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

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 calculate mgs from 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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is used 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.

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

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 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.

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

Benzene

Analyte:	Benzene	Method No.:	S311
Matrix:	Air	Range:	13-51.8 ppm
OSHA Standard:	Ceiling - 25 ppm Peak - 50 ppm 8-hr. T.W.A. - 10 ppm	Precision ($\overline{CV}_T$):	0.059
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	4/23/76

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 13-51.8 ppm at an atmospheric temperature and pressure of 24°C and 762 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 2.5-100 ppm. 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 benzene and other substances in the air. The first section of the charcoal tube was found to hold at least 6.8 mg of benzene when a test atmosphere containing 149.1 mg/cu m of benzene in air was sampled at 0.19 liter per minute for 240 minutes; breakthrough was not observed at this time since no benzene was detected in the backup section of the charcoal tube.

(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. Interferences

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

3.3 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 13-51.8 ppm was 0.059. This value corresponds to a 1.5 ppm standard deviation at the OSHA ceiling 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 ceiling standard level using the overall sampling and analytical method were 0.8% 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 Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ± 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 (3-ft x 1.8-in. O.D. 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 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: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Benzene, reagent grade.

7.3 Hexane, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 nearer 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 At the ceiling concentration, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow rate of 0.20 liter per minute.

8.3.6 At the 8-hour time weighted average concentration, a sample size of 12 liters is recommended. Sample at a flow rate of 0.20 liter per minute.

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

8.3.8 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.9 With each batch of ten samples submit one tube from the same lot of tubes 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 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.11 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. 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. 200°C injector temperature
5. 265°C manifold temperature (detector)
6. 115°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 evaporation of solvent

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 (100 mg) is measured into a 64 mm, 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 a hexane solution of benzene containing 43.9 ng/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample 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 2-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the OSHA ceiling 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. These standards are used to confirm the calibration of the gas chromatograph.

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/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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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 CDC-99-74-45.

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

Cadmium Dust

Analyte:	Cadmium	Method No.:	S312
Matrix:	Air	Range:	0.12-0.98 mg/cu m
OSHA Standard:	0.6 mg/cu m-Ceiling 0.2 mg/cu m-TWA	Precision ($\overline{CV}_T$):	0.064
		Validation Date:	6/18/76
Procedure:	Filter collection Acid digestion Atomic absorption		

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix; cadmium and its compounds are then solubilized in a hydrochloric acid solution maintained at a pH of 1.

1.2 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for cadmium is used to provide a characteristic cadmium line at 228.8 nm. The absorbance is proportional to the cadmium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.12-0.98 mg/cu m at an atmospheric temperature and pressure of 23°C and 759 mm Hg, using a 25-liter sample.

2.2 The OSHA standard for cadmium has an acceptable 15-minute ceiling value. Sampling at a nominal flow rate of 1-2 liters per minute for 15 minutes will yield 15-30 liters of air sample. For a sample size of 15 liters, the working range of the method is estimated to be 0.2-2 mg/cu m; for a sample size of 30 liters, the range is estimated to be 0.1-2 mg/cu m.

2.3 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

3.1 There are no known spectral line interferences for the cadmium AA assay.

3.2 Fe does not interfere with the AA analysis even when present in the proportion of 1 part Cd to 22 parts Fe.

3.3 Cadmium exhibits strong self-absorption at 228.8 nm. It is necessary to operate the cadmium hollow cathode lamp at relatively low currents to prevent self-absorption, although higher currents can be used with some lamps containing a cadmium alloy cathode (Reference 11.4).

3.4 Silicon has been reported (Reference 11.4) to interfere with the cadmium assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.12-0.98 mg/cu m was 0.064. This value corresponds to a 0.04 mg/cu m standard deviation at the OSHA acceptable ceiling concentration. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the filters was 105%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple and specific for cadmium.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for an air-acetylene flame.

6.3.1 Cadmium hollow cathode lamp

6.3.2 Air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25-ml volumetric flasks

6.5 A[illegible]ustable thermostatically controlled hot plate capable [illegible] reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Hydrochloric acid, 0.5N

7.4 Concentrated hydrochloric acid

7.5 Aqueous standard stock solutions containing 100 µg/ml of cadmium (commercially available). This solution can also be prepared by dissolving 1.000 g Cd metal in a minimum amount of nitric acid and diluting to 1.0 liter.

7.6 Cadmium working standard solution, 10 µg/ml. Prepare by appropriate dilution of above solution. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect cadmium dusts, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1-2 liters per minute with face cap on and small small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers. Transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this

process two more times using 2 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to dryness.

8.3.3 Cadmium dissolution. To ensure complete dissolution of cadmium, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). This is done by adding 2 ml of concentrated HCl and evaporating to about 0.5 ml; this HCl addition and evaporation step is done three times. Do not allow the solution to evaporate to dryness at any point.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 5-ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.7 Dilute all samples to 25 ml with distilled water.

8.3.8 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 228.8 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.4 than is necessary to effect a quantitative transfer.

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

8.3.9 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

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

8.4.2 **Procedure for determining recovery.** An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 25-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) were spiked accordingly by adding an aliquot of a solution of cadmium nitrate containing known amounts of cadmium. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 105%.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 From the standard cadmium working standard solution, prepare at least six calibration standards to cover the cadmium concentration range from 3 to 60 µg per 25 ml. Prepare these calibration standards fresh daily and make all dilutions with 0.5N HCl.

9.2 Proceed as in Section 8.3.8.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

μg sample = μg found in sample filter
μg blank = μg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample

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

10.4 If unusual temperatures and pressures were encountered during sampling, convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = Volume of air in liters at 25°C and 760 mm Hg
V = Volume of air in liters as measured
P = Barometric pressure in mm Hg
T = Temperature of air in °C

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{V_s}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

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

11.4 Christian, Gary and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., pp. 355-56, 1970.

Cadmium Fume

Analyte:	Cadmium	Method No.:	S313
Matrix:	Air	Range:	0.04 - 0.175 mg/cu m*
			0.122 - 0.57 mg/cu m$^{\Delta}$
OSHA Standard:	0.1 mg/cu m - TWA		
	0.3 mg/cu m - Ceiling	Precision ($\overline{CV}_T$):	0.062*
			0.060$^{\Delta}$
Procedure:	Filter collection,		
	Acid digestion,	Validation Date:	11/26/76
	Atomic absorption		

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix; cadmium and its compounds are then solubilized in a hydrochloric acid solution maintained at a pH of 1.

1.2 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for cadmium is used to provide a characteristic cadmium line at 228.8 nm. The absorbance is proportional to the cadmium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.122-0.57 mg/cu m at an atmospheric temperature and pressure of 24°C and 759 mm Hg, using a 25-liter sample. The method was also validated over the range of 0.042-0.175 mg/cu m for a 140-liter sample at 20°C and 770 mm Hg atmospheric temperature and pressure.

2.2 The OSHA standard for cadmium has a 15-minute ceiling value. Sampling at a nominal flow rate of 1.5 liters per minute for 15 minutes will yield approximately 25 liters of air sample. For a sample size of 25 liters, the working range of the method is estimated to be 0.1-2 mg/cu m; for a sample size of 140-liters, collected over 1.5 hrs, the range is estimated to be 0.02-0.4 mg/cu m.

2.3 The method may be extended to higher values by further dilution of the sample solution; the absolute sensitivity of the method has not been established.

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* For a 140-liter sample.

$^{\Delta}$ For a 25-liter sample.

3. Interferences

3.1 Iron does not interfere with the AA analysis even when present in the proportion of 1 part cadmium to 22 parts iron (Reference 11.1).

3.2 Cadmium exhibits strong self-absorption at 228.8 nm. It is necessary to operate the cadmium hollow cathode lamp at relatively low currents to prevent self-absorption, although higher currents can be used with some lamps containing a cadmium alloy cathode (Reference 11.2).

3.3 Silicon has been reported (Reference 11.2) to interfere with the cadmium assay.

3.4 Cadmium dust (OSHA standard = 0.2 mg/cu m) and other particulate cadmium compounds would interfere with the analysis. The sample source and the particle size can be used as a guideline to distinguish cadmium fume and cadmium dust. An acceptable particle size cut-off designation is: (fumes) < 1 micrometer > (dust). In terms of source, fumes usually result from chemical reactions, such as oxidation, or from sublimation or distillation processes followed by condensation, while dusts are generally formed by disintegration processes, such as those typically found in mining and ore-reduction operations. (Reference 11.3).

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.04-0.18 mg/cu m was 0.062 and 0.060 in the range of 0.12-0.57 mg/cu m. These values correspond to a 0.006 mg/cu m standard deviation at the OSHA TWA concentration and to an 0.02 mg/cu m standard deviation at the OSHA ceiling concentration. Statistical information and details of the validation and experimental test procedures can be found in References 11.4 and 11.5.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the filters was 103%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple and specific for cadmium but will not distinguish between cadmium dust and cadmium fume.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of a filter medium and support pad (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Barometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter. 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for an air-acetylene flame.

6.3.1 Cadmium hollow cathode lamp

6.3.2 Air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used

6.4 Glassware, borosilicate

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipetes, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards

6.4.3 25-ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Water, distilled or deionized

7.2 Nitric acid, concentrated

7.3 Hydrochloric acid, 0.5N

7.4 Hydrochloric acid, concentrated

7.5 Aqueous standard stock solutions containing 1000 µg/ml of cadmium (commercially available). This solution can also be prepared by dissolving 1.000 g Cd metal in a minimum amount of nitric acid and diluting to 1.0 liter with 0.5N HCl.

7.6 Cadmium working standard solution, 10 µg/ml. Prepare by appropriate dilution of above solution. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

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

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Collection and Shipping of Samples

8.2.1 To collect cadmium fume, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1-2 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process two more times using 2 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to dryness.

8.3.3 Cadmium dissolution. To ensure complete dissolution of cadmium, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). This is done by adding 2 ml of concentrated HCl and evaporating to about 0.5 ml; this HCl addition and evaporation step is done three times. Do not allow the solution to evaporate to dryness at any point.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 5-ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.7 Dilute all samples to 25 ml with distilled water.

8.3.8 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 228.8 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.4 than is necessary to effect a quantitative transfer.

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

8.3.9 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

8.4.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the

recovery of the compound. The sample recovery should be determined in duplicate at each test level chosen so as to cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

- Procedure for determining recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 25-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA ceiling standard) were spiked accordingly by adding an aliquot of a solution of cadmium nitrate containing known amounts of cadmium. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 103%.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 From the standard cadmium working standard solution, prepare at least six calibration standards to cover the cadmium concentration range from 1 to 60 µg per 25 ml. Prepare these calibration standards fresh daily by dilution of appropriate aliquots of the working standard solution using 0.5 N HCl for all dilutions.

9.2 Proceed as in Section 8.3.8.

9.3 **Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.**

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

10.2 Corrections for the blank must be made for each sample

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

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

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

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

where:

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

10.5 The concentratration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

11.1 Cadmium Dust, S312, Backup Data Report prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

11.2 Christian, Gary and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., pp. 355-56, 1970.

11.3 Dennis, Richard, Ed., Handbook on Aerosols, Technical Information Center, Office of Public Affairs, U.S. Energy Research and Development Administration, 1976, pp. 2-3.

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

11.5 S313 Backup Data Report for Cadmium Fume, prepared under NIOSH Contract No. 210-76-0123, 11/26/76.

11.6 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1971.

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

Carbon Tetrachloride

Analyte:	Carbon Tetrachloride	Method No.:	S314
Matrix:	Air	Range:	65-299 mg/cu m
OSHA Standard:	25 ppm (160 mg/cu m)-Ceiling 10 ppm (65 mg/cu m)-T.W.A.	Precision ($\overline{CV}_T$):	0.092
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 65-299 mg/cu m at an atmospheric temperature and pressure of 27.2°C and 761 mm Hg, using a 17-liter sample. Under the conditions of recommended sample size (15 liters) the probable useful range of this method is 16-480 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7.5 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 15 mg of analyte when a test atmosphere containing 322 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

(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 as 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 65-299 mg/cu m was 0.092. This value corresponds to a 15-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 7.8% 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" concentrations. Therefore, no recovery correction should be applied to the final result.

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

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 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, graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Carbon Tetrachloride, reagent grade

7.3 Decane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 For determining the ceiling and peak concentrations, a sample size of 5 liters is recommended. Sample for 5 minutes at a flow of 1.0 liters per minute. For determining the T.W.A. concentration, a sample size of 15 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 155°C injector temperature
5. 200°C manifold temperature (detector)
6. 60°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the OSHA ceiling) are prepared by adding an amount of analyte equivalent to that present in a 15-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

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

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 per 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 per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

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

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

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

where:

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

11. References

11.1 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.

Silica, Crystalline

Analyte:	Crystalline Silica (Quartz, Cristobalite, Tridymite)	Method No.:	S315
Matrix:	Air	Range:	0.167-0.846 mg/cu m as respirable quartz for a sample containing 29.35% SiO_2
OSHA Standard:	Dependent on % SiO_2*	Precision ($\overline{CV}_T$):	0.065
Procedure:	Collection on filter, X-ray diffraction analysis	Validation Date:	2/27/76

1. Principle of the Method

1.1 A known volume of air is drawn through a silver membrane filter to collect crystalline silica.

1.2 The filter samples are scanned by X-ray diffraction to determine the presence of crystalline silica polymorphs (quartz, cristobalite and tridymite) and other phases that cause matrix interference.

1.3 The mass of each crystalline silica polymorph present is determined by measuring the diffraction peak intensity of the polymorph and of the silver filter. The mass is calculated from calibration data. (Reference 11.1)

1.4 The current format of the OSHA standard requires knowing the free silica (% SiO_2) content of the sample. This determination is carried out by analysis of the bulk air sample, using this X-ray diffraction procedure. A 2-mg portion of the bulk air sample is used to prepare a suspension of the bulk air sample in isopropyl alcohol; this suspension is used to prepare the silver membrane filter loaded with the bulk air sample. (Refer Section 8.5.)

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* The OSHA standard for the various silica polymorphs are expressed as:

$$\text{Quartz (respirable)} = \frac{10 \text{ mg/cu m}}{\% \ SiO_2 + 2}$$

$$\text{Quartz (total)} = \frac{30 \text{ mg/cu m}}{\% \ SiO_2 + 2}$$

Cristobalite and tridymite = 1/2 value calculated for quartz.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.167-0.846 mg/cu m (quartz, respirable) using a sample of granite dust known to contain 29.35% SiO_2 (Reference 11.2). The sample size collected was 200 liters at atmospheric temperature and pressure in the range of 24-28°C and 760-764 mm of Hg.

2.2 The method may be extended to higher sample concentrations by collecting a smaller sample volume in order to prevent collection of too much sample particulate. Collection of too much sample is undesirable not only because it can bring about loss of collected sample through flaking off the filter but also because of the probability of sample X-ray absorption which would prevent accurate intensity measurement of the underlying filter.

2.3 For the studies cited in Reference 11.3, the method was evaluated for the range of 14-303 µg quartz present in respective dust samples weighing 34-1226 µg. For screening an unknown sample, the presence of 15 µg or more of quartz, 25 µg or more of cristobalite, and 15 µg or more of tridymite can be determined by an X-ray diffraction scan; once the polymorph has been established to be present in the sample, the method can be used to determine as little as the following total microgram loading on a 25-mm silver filter--5 µg quartz, 15 µg cristobalite and 10 µg tridymite. The method has been demonstrated for a collected mass of 1.3 mg.

3. Interferences

3.1 Several minerals have diffraction peaks that interfere with the major peak for quartz; these include micas (biotite, muscovite), potash, feldspars (microcline, plagioclase), sillimanite, graphite, iron carbide (FeC), and zircon. Comparable matrix interference may occur for cristobalite and tridymite. The presence of matrix phase interference can be verified by X-ray diffraction analysis. In this case, analytical measurements are made using a secondary peak of the crystalline silica polymorph, with a commensurate decrease in detection limit and precision.

3.2 The presence of specific elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analysis method for quartz (respirable) in the range of 0.167-0.85 mg/cu m was 0.065. This value corresponds to a 0.021 mg/cu m standard deviation at the OSHA standard level for quartz in respirable samples containing 30% SiO_2. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.4.

4.2 A collection efficiency of 100% was determined for the collection medium at the 2X level; thus, no bias was introduced in the sample collection step. Likewise, no significant bias in the analytical method is expected beyond the errors associated with the X-ray measurement. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

4.3 The results of the experimental studies described in Reference 11.1 showed that for quartz in the range of 14 to 38 µg, the $\overline{CV}_T$ for the total sampling and analysis method was 0.13 vs 0.04 for the range of 49 to 303 µg.

4.4 The precision and accuracy of the method for cristobalite and tridymite have not been determined.

5. Advantages and Disadvantages of the Method

5.1 The X-ray diffraction method is specific for the individual polymorphs with sensitivity equivalent to or greater than other methods (infrared and colorimetric). The method is non-destructive, rapidly performed, reduces sample manipulation to a minumum and may be automated.

5.2 Application of the method requires an experienced analyst.

6. Apparatus

6.1 Sampling Equipment. The required sampling equipment consists of the accessory items needed to collect personal samples and the bulk air sample. The items needed in each case are listed in Sections 6.1.1 and 6.1.2.

6.1.1 For each personal sample, use a 10-mm nylon cyclone, a filter unit consisting of the silver membrane filter (Section 6.2) and appropriate 25-mm two-piece cassette filter holder, a personal sampling pump calibrated with a representative filter and filter holder in the line and whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.1.2 For the bulk air sample, use a 1-inch HASL cyclone (Bendix No. 240 cyclone), a 47-mm fluoropore filter (1 micrometer pore size) contained in a 47-mm filter holder, and a properly calibrated Gast 1022 vacuum pump equipped with an appropriate needle valve flow controller.

6.2 Silver membrane filter, 1.2 µm pore size and 25 mm diameter. The filter is held in the two-piece cassette by a stainless steel backup screen and a Teflon gasket.

6.3 X-ray diffraction equipment with a copper target X-ray tube.

6.4 Microbalance.

6.5 Dust generation chamber (Reference 11.3) or filtration apparatus, ultrasonic stirrer and 1000 ml polyethylene bottles for preparing calibration standards.

6.6 Chip of mica (~0.5 sq. mm by 0.02 mm thick) glued to an aluminum plate or equivalent, for use as an instrument calibration standard.

6.7 Storage chamber with desiccant.

6.8 Filter storage cassettes.

6.9 Non-serrated, non-magnetic forceps.

6.10 Volumetric flask, 1-liter capacity.

6.11 Ultrasonic agitator.

6.12 Graduated cylinder, 250 ml or convenient size.

6.13 Filtration Unit - Pyrex microanalysis with frit support and clamp.

6.14 Filter flask, 500 ml or convenient size.

6.15 PetriSlide (Millipore) or a plastic Petri dish to hold the filter samples.

6.16 Flow Meter.

7. Reagents

7.1 Quartz, cristobalite and tridymite powders: acid-washed with 9 N nitric acid and wet-sieved through a 10-μm sieve. Quartz powder has been obtained from Wedron Silica Co., cristobalite and tridymite have been obtained from the Bureau of Mines.

7.2 Parlodion, 1% in amyl acetate. This is used for permanently fixing the silica to the filters used for calibration standards.

7.3 Isopropyl Alcohol.

7.4 Desiccant (Drierite).

8. Procedure

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

8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This

will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and shipping of samples

8.3.1 To collect a personal sample, assemble the filter and two-piece filter cassette and tighten firmly to insure that the gasket seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded.

8.3.2 Remove the cassette's plugs and attach the outlet of the cyclone to the inlet of the cassette. The cyclone's body, the cyclone's vortex finder and the filter cassette must remain aligned and firmly in contact. The outlet of the filter holder is connected to the pump by a short piece of flexible tubing.

8.3.3 Air being sampled should only be passed through the cyclone before entering the filter cassette. The cyclone acts as a particle size separator and will allow only the respirable particles to pass through and collect on the filter.

8.3.4 Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Position the middle of the rotameter ball of the personal sampling pump to the 1.7 liter per minute calibration mark as accurately as possible. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

8.3.5 Collected sample cassettes should be firmly sealed with the plugs in both the inlet and outlet.

8.3.6 Carefully record sample identity and all relevant sample data.

8.3.7 Blank. With each batch of samples, submit twelve filters from the same lot as that used for sampling and which are subjected to exactly the same handling as for the samples except that no air is drawn through these filters. Label these as blanks or clean filters. These clean filters are necessary for proper sample analysis.

8.3.8 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3.9 Bulk Sample. Two bulk samples must be collected--a "rafter or settled dust" bulk sample and a respirable bulk air sample.

1. To collect the "rafter or settled dust" bulk sample, fill a 20-ml glass vial with dust found on rafters or any other place within the premises being sampled.

2. To collect the respirable bulk air sample, the following items are needed: a vacuum pump with a capacity of 75 liters per minute at 15 inches of Hg vacuum; a 75 liter per minute critical flow orifice; a 47-mm diameter Teflon filter with a pore size of 1.0 micrometer; a 47-mm diameter filter holder; a 1-inch diameter HASL cyclone (Bendix No. 240 cyclone or equivalent); and 1/2-inch diameter vacuum tubing. The critical flow orifice must have been calibrated with a representative sampling train in line.

3. Select a sampling site that is representative of the workers' environment.

4. After assembling filter and filter holder, connect the inlet of the filter holder to the cyclone's outlet with a short piece of tubing. The critical flow orifice is inserted in the vacuum tubing between the pump and the filter.

5. Turn the pump on and sample at a rate of 75 liters per minute. At least 2 milligrams of respirable dust must be collected. Consequently, the filter must be overloaded and sampling is not terminated when a prefilter cake is formed. Therefore, a sampling time of at least 6 hours is recommended.

8.4 Sample Analysis

8.4.1 Carry out X-ray diffraction analysis of the bulk air sample to determine the presence of crystalline (free) silica polymorphs and any matrix interference. Alternatively, the "rafter or settled dust" samples could be used for this purpose.

8.4.2 Open the cassette filter holder, remove the silver filter with forceps and secure to an aluminum (or magnesium) sample holder for the diffractometer.

8.4.3 Insert into the diffractometer and scan over the range corresponding to d = 4.5 to 2.34° (18 to 40° in 2θ for CuK_α radiation). The presence of crystalline (free) silica polymorphs is determined by the presence of diffraction peaks as follows:

	2θ (CuK_α)	
Phase	Primary Peak	Secondary Peak(s)
Quartz	26.66	20.85
Cristobalite	21.9	
Tridymite	20.6	23.4, 21.7
Silver	38.1	44.3

The presence of interfering compounds can be determined by identifying other X-ray diffraction peaks and by reference to the bulk sample analysis (Section 8.4.1).

8.4.4 The most intense diffraction peak of each crystalline (free) silica polymorph that is free from matrix interference is analyzed by hand peaking (or scanning) to the maximum intensity and measuring intensity by the fixed time scaler mode. A comparable measurement is made for background intensity at a nearby position selected by reference to the diffraction scan (Section 8.4.3). The measured peak intensity is then corrected for background. A comparable set of measurements is made for a peak from the silver filter.

8.4.5 If there is matrix interference with all usable diffraction peaks for the crystalline (free) silica polymorphs (Section 8.4.3), the level of interference must be determined from the relative intensity of other diffraction peaks associated with the interfering phase for correcting the measured crystalline (free) silica polymorph intensity.

8.4.6 At periodic intervals (every four to six samples), peak (2θ-26.9 for CuK_α radiation) and background intensities are collected for the mica calibration standard by the procedure described in Section 8.4.4.

8.4.7 All intensity values are recorded on a suitable analysis data sheet.

8.5 Determination of % SiO_2 in Bulk Air Sample

8.5.1 Preparation of alcohol suspension of bulk sample

1. Scrape off a portion of the bulk air sample collected on the 47-mm fluoropore filter and submitted to the laboratory with each batch of personal samples. Accurately weigh 2.00 mg of this bulk air sample.

2. Quantitatively transfer the weighed sample into a 1-liter volumetric flask. Treat this sample with approximately 50-100 ml of isopropyl alcohol. Do not dilute to volume at this point.

3. Put the flask in an ultrasonic agitator for 10 minutes. Cool flask to room temperature before dilution to volume.

4. Dilute to the 1-liter mark with more isopropyl alcohol and leave in the ultrasonic agitator for another 30 minutes. Cool to room temperature and add more isopropyl alcohol, if necessary. Note: Manually shake this suspension which will be used to prepare the filters loaded with the bulk sample, before taking any aliquot.

8.5.2 Preparation and Analysis of filter loaded with bulk sample.

1. A tared 25 mm silver membrane filter is placed in position between the funnel section and frit support of the filtration unit assembly and the unit is secured together with a clamp.

2. Attach the filtration unit assembly to a filter flask and add 15 ml of neat isopropyl alcohol into the filter funnel. This isopropyl alcohol level is added before beginning the filtration of the suspension in order to aid in the preparation of a uniformly loaded filter.

3. Manually shake or agitate the stock suspension and measure 250 ml of the bulk <u>air</u> sample suspension in a graduated cylinder.

4. Turn on the water-vacuum line and immediately begin the filtration of the 250 ml of bulk sample suspension by adding into the filter funnel. A liquid head must be maintained above the filter throughout the filtration cycle inclusive of the stage when the graduated cylinder is rinsed with more isopropyl alcohol and filtered to effect complete sample transfer. If the filter is allowed to run dry <u>during</u> the filtration cycle, a non-uniform distribution of sample on the filter can occur which can cause errors in the sample analysis.

5. When the final rinsing has been added, allow the liquid to filter through completely and allow filter to run dry.

6. Carefully remove the filter from the filtration unit and transfer to the PetriSlide holder with the aid of the forceps.

7. Dry the filter in a vacuum oven at 110°C for 60 minutes.

8. Transfer to a desiccator, cool, and weigh.

9. Let stand overnight in a desiccator or put in a vacuum oven for another 10-15 minutes. Cool and weigh again to constant weight.

10. The difference in weight between the filter plus sample and the weight of the filter alone is the sample weight used to calculate % SiO_2 in bulk air sample.

11. Analyze for crystalline (free) silica content as described in Section 8.4.

9. Calibration and Standards

9.1 Crystalline (free) silica standards are prepared by the dust dispersion method.

A dust dispersion chamber, such as described in References 11.3 and 11.4, is used to prepare the appropriate standards. Standards are prepared by individually dispersing quartz, cristobalite and tridymite into an air stream which is fed into a mixing chamber after adding dilution air and removing electrostatic charge. Approximately ten dust samples are collected simultaneously on tared silver membrane filters (25 mm diameter, 1.2 µm pore size). Several sets of standards should be prepared for each polymorph within the range 20-300 µg silica per filter.

9.2 The filter calibration samples are desiccated over drierite for 24 hours and weighed to yield the mass of free silica phase on each filter. After weighing, the powder is permanently attached to the filter by the following process.

9.2.1 Place a piece of screen in a Petri dish, cover with a piece of filter paper and fill the dish to the level of the filter paper with 1% parlodion in amyl acetate.

9.2.2 Place a silver membrane filter (dust side up) on the paper. Capillary forces will draw the parlodion solution through the silver filter, wetting the top surface.

9.2.3 When completely wetted, remove the silver filter and allow to dry.

9.3 For each standard filter, the crystalline (free) silica peak and silver peak intensities are measured by the procedure described in Section 8.4.4.

9.4 Intensity measurements are made for ten clean silver membrane filters (see Section 8.3.7) alternated with ten measurements on the mica instrument calibration standard.

9.5 A calibration constant K° is determined for the principal diffraction line of each crystalline (free) silica phase by the following expression:

$$K^\circ = \frac{I_M^*}{i} \sum_{\circ}^{i} \frac{W_S^\circ}{A^\circ I_S^\circ}$$

where:

I_S° = intensity of the crystalline (free) silica standard

W_S° = mass of crystalline (free) silica standard in µg

A° = effective area of filter (sq cm)

i = number of standard filters in set

I_M^* = average intensity of the mica calibration sample as determined in Section 9.4.

It is recommended that each laboratory performing this analysis should determine a historical average K° value.

10. Calculations

10.1 Test for sample X-ray absorption based on the equation:

$$T_{Ag} = \frac{I_{Ag}}{C\ I_M}$$

where:

T_{Ag} = sample transmittance determined based on relative intensity of underlying silver filter between sample and clean filters.

I_{Ag} = intensity of the underlying silver filter.

I_M = intensity of the mica instrument calibration standard.

$C = I_{Ag}^*/I_M^*$

where:

I_{Ag}^* = average intensity of clean silver filters as determined in Section 9.4

I_M^* = average intensity of the mica calibration standard as determined in Section 9.3.

10.2 Determine the mass of each crystalline (free) silica phase in the sample by using either of the two expressions below depending on the value of T_{Ag}.

For $T_{Ag} \geq 0.90$:

$$W_S = \frac{K^\circ \cdot I_S \cdot A}{I_M} \qquad \text{(Eq. 10.2.1)}$$

For $T_{Ag} < 0.90$:

$$W_S = \frac{-R\,K^\circ \cdot I_S \cdot A \cdot \ln T_{Ag}}{I_M \left(1-T_{Ag}^{\,R}\right)} \qquad \text{(Eq. 10.2.2)}$$

where:

W_S = mass of crystalline (free) silica phase in the sample in µg

K° = calibration constant as in Section 9.5

I_S = intensity of crystalline (free) silica phase

A = effective area of the sample collection filter (sq. cm)

I_M = intensity of the mica instrument calibration standard

$$R = \frac{\sin\theta_{Ag}}{\sin\theta_S}$$

where:

θ_{Ag} = diffraction angle for silver

θ_S = diffraction angle for the crystalline (free) silica line and polymorph

10.3 Corrections for the blank (determined for each of the polymorphs--quartz, cristobalite and tridymite) must be made for each sample.

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

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.4 For personal sampling pumps with rotameters only, the following correction for air volumes sampled should be made:

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

where:

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

10.5 The concentration of the crystalline (free) silica in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\mu g \ SiO_2/\text{liter} = \frac{\mu g \ Q + \mu g \ C + \mu g \ T}{V_S}$$

μg Q = micrograms of quartz
μg C = micrograms of cristobalite
μg T = micrograms of tridymite

10.6 The % crystalline (free) silica of the bulk air sample is determined by dividing the mass of crystalline (free) silica found by the sample weight taken.

$$\% \ SiO_2 = \frac{\text{mg crystalline silica}}{\text{mg bulk air sample}} \times 100$$

The mg values needed are determined as described in Section 8.5.2.

11. References

11.1 Leroux, J., Davey, A., and Paillard, A., "Proposed Standard Methodology for the Evaluation of Silicosis Hazards," Amer. Ind. Hyg. Assoc. J. 34, 409 (1973).

11.2 Talvitie, N.A., "Determination of Free Silica: Gravimetric and Spectrophotometric Procedures Applicable to Airborne and Settled Dust," Amer. Ind. Hyg. Assoc. J. 25, 169 (1964)

11.3 Peters, E.T., "Evaluation of the NIOSH X-ray Diffraction Method for the Determination of Free Silica in Respirable Dust," Final Report to NIOSH, Contract No. CDC-99-74-51, (May, 1976).

11.4 Crystalline Silica, No. S315, Backup Data Report, prepared under NIOSH Contract No. CDC-99-74-45, submitted in October, 1976.

Chromic Acid and Chromates

Analyte:	Chromic Acid and Chromates	Method No.: S317
Matrix:	Air	Range: 0.052-0.204 mg/cu m
OSHA Standard:	0.1 mg/cu m (as CrO_3)-Ceiling	Precision ($\overline{CV}_T$): 0.084
Procedure:	Filter collection; dilute acid leaching; colorimetric determination of complexed Cr(VI)	Validation Date: 10/24/75

1. Principle of the Method (References 11.1-11.3)

   1.1 A known volume of air is drawn through a polyvinyl chloride (PVC) filter to collect the analyte.

   1.2 The analyte is extracted from the filter with 0.25 M sulfuric acid, diphenylcarbazide is added, and additional acid is added to bring the volume to 20 ml.

   1.3 The absorbance of the solution at 540 nm is used as a quantitative measure of the analyte.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.052-0.204 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg, using a 15-minute sample. Under the conditions of the sample size (22.5 liters), the linear working range of the method is estimated to be 0.025-0.6 mg/cu m CrO_3.

   2.2 When using a 5-cm cell and a final volume of 20 ml for a 22.5-liter sample, the sensitivity is estimated to be 0.01 mg/cu m CrO_3.

3. Interferences

   Possible interferences for the diphenylcarbazide method include many of the heavy metals. The ones likely to be encountered at appreciable levels are iron, copper, nickel, and vanadium. Tests show that 10 micrograms of any of these give less than or equal to that obtained from 0.04 microgram CrO_3.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.052-0.204 mg/cu m was 0.084. This value corresponds to a 0.008 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 11.4.

4.2 A collection efficiency of 0.945, standard deviation of 0.035, was determined for the collection medium and a correction for collection efficiency should be made in Section 10.5. $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method since there are no apparent biases for which corrections have not been made.

5. Advantages and Disadvantages of the Method

5.1 The method is simple, specific, and sensitive. The samples collected on PVC filters are stable.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the filter collection method has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a two- or three-piece filter cassette.

6.1.2 Personal Sampling Pump. A personal sampling pump whose flow can be determined to an accuracy of ±5% at a sampling rate of 1.5 liter per minute. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 VMI (Gelman) 37-mm diameter and 5.0 micrometer pore size PVC filters or equivalent.

6.3 Spectrophotometer. This instrument should be capable of measuring the developed color at 540 nm.

6.4 Matched glass cells or cuvettes, 5-cm path length.

6.5 All polypropylene or Teflon forceps.

6.6 Assorted laboratory glassware--pipets, volumetric flasks, large test tubes, and graduated cylinders of appropriate capacities.

6.7 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.

6.8 Buchner funnel.

7. Reagents

All reagents must be analytical reagent grade or better.

7.1 Sulfuric acid, 0.25 M. Add 14 ml of concentrated sulfuric acid to some distilled water in a one liter volumetric flask and dilute to mark. For uniformity of results it is suggested that the same solution be used for all samples, blanks, and standards. After thorough mixing, it is convenient to transfer part of the solution to a small plastic wash bottle.

7.2 Diphenylcarbazide. Dissolve 0.50 g of sym-diphenylcarbazide in a mixture of 100 ml of acetone and 100 ml of double distilled water. Store in a dark bottle in the refrigerator. This solution is good for up to one month.

7.3 Chromium (VI) standard. Dissolve 0.2829 g of potassium dichromate in water in a 1-liter volumetric flask and dilute to mark. This solution is 100 ppm (by weight) of chromium (VI). The chromium (VI) concentration can also be expressed as 0.1 microgram/microliter.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Wash all glassware in hot, soapy water, and follow with tap and distilled water rinses.

8.1.2 After initial cleaning, soak glassware in concentrated nitric acid (10% nitric acid for plastics) for 30 minutes. Rinse thoroughly with tap water, distilled water, and double 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 filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PVC 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 15-minute sample 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 PVC filter should be removed from the cassette filter holder and the cellulose backup pad within 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 Pipet 20 ml of water into each of six large test tubes. Put a piece of tape on the test tube so that the bottom of the tape matches the meniscus. Rinse and dry the test tubes.

8.4.2 To facilitate the analysis of the sample and to remove the possibility of interferences from suspended dusts, a simple apparatus may be constructed. A two-hole stopper sufficiently

large to fit the test tubes described in Section 8.4.1, if altered by enlarging one hole, can accommodate a small Buchner funnel and vacuum line. Remove the filter from the screw cap bottle and place the filter in the Buchner funnel. Cover the filter with 5 ml 0.25 M sulfuric acid and allow to stand for 5 minutes. Rinse the screw cap bottle with 2-3 ml of 0.25 M sulfuric acid. Using the vacuum, wash the filter with another 5-7 ml of 0.25 M sulfuric acid and filter the solution into the test tube. After the solution has filtered through, remove the filter and wash the funnel with several milliliters of 0.25 M sulfuric acid. Standards should be set up along with each set of samples being analyzed. Also, a blank filter through which no air has been drawn, should be analyzed along with the samples.

8.4.3 Add 0.5 ml of the diphenylcarbazide solution to each test tube. Then add additional 0.25 M sulfuric acid until the meniscus matches the bottom edge of the tape.

8.4.4 Shake the test tube to mix and transfer to a clean, dry 5-cm cell for analysis.

8.4.5 Read the absorbance of the solution on a spectrophotometer at 540 nm against a blank prepared from 0.25 M sulfuric acid in the same fashion as for the samples.

9. Calibration and Standards

9.1 Transfer 6 or 7 ml of 0.25 M sulfuric acid into each of six 5-cm cells. Pipet 5 , 10, 20, 50, and 100 microliters of the 100 ppm standard (Section 7.3) into the six cells, respectively. Process one cell as a blank. Add 0.5 ml of the diphenylcarbazide solution and sufficient 0.25 M sulfuric acid to bring to the 20-ml mark. Shake and wipe clean. Adjust the baseline of the spectrophotometer to zero by reading distilled water. Read the blank, then read the five standards at 540 nm.

9.2 A calibration curve is drawn by plotting the absorbance of the standards against microgram of chromium (VI) in the colored solution.

10. Calculations

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

10.2 Determine from the calibration curve (Section 9.2) the micrograms of CrO_3 present in each sample.

10.3 The concentration of the analyte in the air sampled can be

expressed in mg/cu m (mg/cu m = microgram/liter).

$$\text{mg/cu m} = \frac{\text{microgram } CrO_3 \text{ (Section 10.2)}}{\text{Air volume sampled (liter)}}$$

10.4 Divide the concentration of the analyte (mg/cu m) by the collection efficiency. (Note: The collection efficiency, when sampled at an atmosphere containing 0.192 mg/cu m at 1.5 liters per minute was determined to be 0.945.)

$$\text{Corr. mg/cu m} = \frac{\text{Concentration of analyte (Section 10.3)}}{\text{Collection Efficiency}}$$

11. References

11.1 Snell and Snell, Colorimetric Methods of Analysis, Volume 11A, D. Van Nostrand Company, pp. 212-215.

11.2 Jacobs, M. B., The Analytical Toxicology of Industrial Poisons, Interscience Publishers, pp. 396-402.

11.3 Abell, M. T. and J. R. Carlberg, "A Simple Reliable Method for Determination of Airborne Hexavalent Chromium," Amer. Ind. Hyg. Journal, 35, No. 4, (April 1974), 229.

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

Xylene
(Xylol)

Analyte:	Xylene	Method No.:	S318
Matrix:	Air	Range:	218-870 mg/cu m
OSHA Standard:	100 ppm (435 mg/cu m)	Precision ($\overline{CV}_T$):	0.060
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	4/23/76

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 218-870 mg/cu m at an atmospheric temperature and pressure of 24°C and 761 mm Hg, using a 12-liter sample. Under the conditions of sample size (12 liters), the probable useful range of this method is 45-1300 mg/cu m. 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 xylene and other substances in the air. The first section of the charcoal tube was found to hold 30 mg of xylene when a test atmosphere containing 870 mg/cu m of xylene in air was sampled at 0.20 liter per minute for 172.6

minutes; breakthrough was observed at this time, i.e., the concentration of xylene 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. Interferences

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

3.3 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 218-870 mg/cu m was 0.060. This value corresponds to a 26 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 2.1% 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 Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ±5% at the recommended flow rate (Reference No. 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 two 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 (3-ft × 1/8-in O.D. 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 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 preparing standards.

6.8 Pipets: 1.0-ml delivery pipets.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Xylene (mixture of isomers), 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 backup and should be positioned nearer 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 12 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 $\pm 5\%$.

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 With each batch of ten samples submit one tube from the same lot of tubes 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.

8.3.9 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 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. 215°C injector temperature
5. 180°C column temperature
6. 275°C detector 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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to

wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 (100 mg) is measured into a 64 mm, 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 the analyte is injected directly into the activated charcoal 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 12-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

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

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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

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

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 CDC-99-74-45.

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

Chromium, Soluble Chromic and Chromous Salts as Cr

Analyte:	Chromium, Soluble Chromic and Chromous Salts as Cr	Method No.:	S323
Matrix:	Air	Range:	0.282-0.947 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.085
Procedure:	Filter collection, nitric acid digestion, atomic absorption	Validation Date:	10/24/75

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

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric acid to destroy the filter and other organic materials in the sample, and the chromium soluble compounds are then dissolved in nitric acid.

   1.3 The solutions of samples and standards are aspirated into the reducing nitrous oxide-acetylene flame of an atomic absorption spectrophotometer (AAS) using a hollow cathode lamp for chromium.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.282-0.947 mg/cu m using a 90-liter sample at an atmospheric temperature and pressure of 22°C and 759 mm Hg. Under the conditions of sample size (90 liters), the working range of the method is estimated to be 0.05-2.5 mg/cu m.

   2.2 The sensitivity of this method for a 90 liter air sample using the 20-ml final solution volume is 0.01 mg/cu m chromium. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   Insoluble chromium compounds which are soluble in concentrated nitric acid may be an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.282-0.947 mg/cu m is 0.085. This value corresponds to a 0.042 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer. The instrument must be equipped with nitrous oxide acetylene burner head.

6.3.1 Chromium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used. Heating tape to warm nitrous oxide regulator during use.

6.4 Glassware, borosilicate:

6.4.1 100-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 3, 5, 7, 10 ml.

6.4.3 100-ml volumetric flasks.

6.4.4 20-ml graduated centrifuge tube.

6.5 Nalgene Bottles

6.5.1 Five 100-ml capacity Nalgene bottles for chromium atomic absorption standards.

6.5.2 One 1000-ml capacity Nalgene bottle for stock chromium atomic absorption standard.

6.6 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Dilute nitric acid (5 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water)

7.4 Potassium dichromate, reagent grade

8. Procedure

8.1 Cleaning of Equipment

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

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

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

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

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

8.4 Analysis of Samples

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

8.4.2 Wet Ashing. Treat the sample in each beaker with 2-3 ml of concentrated nitric acid to destroy the organic filter matrix. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Repeat this step twice. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a fume hood until a white ash appears. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate to dryness.

8.4.3 Cool each beaker and dissolve residues in 1 ml concentrated nitric acid.

8.4.4 Quantitatively transfer the clear solutions to a 20-ml graduated centrifuge tube.

8.4.5 Rinse each beaker at least three times with 2-3 ml portions of distilled or deionized water and quantitatively transfer each rinse to the solution in the centrifuge tube. Dilute all samples to 20 ml with distilled or deionized water.

8.4.6 Aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 357.9 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume such as 5 or 10 ml before aspiration. In such a case use no more acid solution in 8.4.3 than is necessary to effect a quantitative transfer.

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

8.4.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare a 100 μg/ml chromium stock standard by dissolving .2829 g potassium dichromate in dilute nitric acid (Section 7.3) and diluting to 1000 ml.

9.2 From the 100 μg/ml stock chromium standard solution, prepare at least 5 working standards to cover the range from 20 to 200 μg/20 ml. Make all standard solutions in dilute nitric acid and prepare fresh each day and store in 100-ml Nalgene bottles.

9.3 Aspirate each of the standard samples and record the absorptions.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/20 ml. It is advisable to run standards both before and after the analysis on a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/20 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample filter

µg blank = µg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Methyl Chloroform
(1,1,1-Trichloroethane)

Analyte:	Methyl Chloroform	Method No.:	S328
Matrix:	Air	Range:	904-3790 mg/cu m
OSHA Standard:	350 ppm (1900 mg/cu m)	Precision ($\overline{CV}_T$):	0.054
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 904-3790 mg/cu m at an atmospheric temperature and pressure of 26°C and 762.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 190-5700 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 17-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 36.2 mg of analyte when a test atmosphere containing 3790 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 51 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(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 as 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 904-3790 mg/cu m was 0.054. This value corresponds to a 102.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.8% 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.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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% OV-101 stationary phase on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic qual ty carbon disulfide

7.2 Methyl Chloroform (1,1,1-Trichloroethane), reagent grade

7.3 Octane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 of 6 liters is recommended. Sample at a rate 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 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Methylene Chloride

Analyte:	Methylene Chloride	Method No.:	S329
Matrix:	Air	Range:	1700-7100 mg/cu m
OSHA Standard:	1000 ppm (3475 mg/cu m)-Ceiling 500 ppm (1740 mg/cu m)-T.W.A.	Precision (CV_T):	0.073
		Validation Date:	6/6/75
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1700-7100 mg/cu m at an atmospheric temperature and pressure of 25°C and 763 mm Hg, using a 1-liter sample. Under the conditions of sample size (1-liter) the probable useful range of this method is 350-10,400 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 10.4 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 23.3 mg of analyte when a test atmosphere containing 6726 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 18.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data are based on a prior experiment.

(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 as 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 1700-7097 mg/cu m was 0.073. This value corresponds to a 254 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 2.8% 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.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: Separate front and backup glass tubes with both ends of each tube flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D. Each tube contains the appropriate amount of 20/40 mesh activated charcoal. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The front adsorbing tube contains 100 mg of charcoal, the backup tube contains 50 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the tubes 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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 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, graduated in 0.1-ml increments.

6.9 **Volumetric flasks: 10-ml or convenient sizes for making standard solutions.**

7. Reagents

7.1 **Chromatographic quality carbon disulfide**

7.2 Methylene Chloride, reagent grade

7.3 Decane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 tubes 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 **For determining the ceiling and peak concentrations, a maximum sample size of 1.0 liter is recommended; sample for 5 minutes at a flow of 0.2 liters per minute. For determining the TWA concentration, a sample size of 2.2 liters is recommended; sample at a flow of 0.05 liters per minute or less. The flow rates 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 60°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 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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the OSHA ceiling) are prepared by adding an amount of analyte equivalent to that present in a 1.0-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Phenol

Analyte:	Phenol	Method No.:	S330
Matrix:	Air	Range:	9.46-37.8 mg/ 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 st.. ards.

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 $\pm$ 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 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 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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.3) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

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. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Phosphoric Acid

Analyte:	Phosphoric Acid	Method No.:	S333
Matrix:	Air	Range:	0.47-1.93 mg/cu m
OSHA Standard:	1.0 mg/cu m	Precision ($\overline{CV}_T$):	0.055
Procedure:	Filter collection, water leach, complex formation, colorimetric	Validation Date:	8/29/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the phosphoric acid aerosol present.

1.2 The filter is removed from the cassette, transferred into a Phillips beaker, and leached with hot water.

1.3 The leached sample is reacted with sodium molybdate and hydrazine sulfate to form the heteropoly blue complex.

1.4 The absorbance of the resulting solution is determined at 830 nm and is used as a measure of the amount of phosphoric acid present.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.47-1.93 mg/cu m at an atmospheric temperature and pressure of 26°C and 757 mm Hg, using a 90-liter sample. For a nominal sample size (90 liters), the probable useful range of the method is 0.10-2.0 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where absorbance is greater than the limits of the standard curve the samples can be diluted with distilled water after the color development to extend the upper limit of the range.

2.2 A concentration of 0.10 mg/cu m of phosphoric acid can be determined in a 90-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 1 cm cell.

3. Interferences

Airborne particulate salts of phosphoric acid will interfere with this determination.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.47-1.92 mg/cu m is 0.055. This value corresponds to a standard deviation of 0.055 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 ± 0.01 was determined for the collecting medium; thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery for the filters was 99.4%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple and precise but the assay procedure is general for total phosphate.

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of inorganic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a 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 Spectrophotometer, capable of reading at 830 nm.

6.4 Matched glass cells or cuvettes, 1 cm path length.

6.5 Boiling water bath.

6.6 Steambath, or equivalent, maintained at 85-100°C.

6.7 Phillips beakers, 125 ml.

6.8 Assorted laboratory glassware: pipets, volumetric flasks, watchglasses.

7. Reagents

All reagents must be ACS Reagent grade or better.

7.1 Distilled water

7.2 Potassium dihydrogen phosphate solution. Dissolve 0.1389 g of potassium dihydrogen phosphate, KH_2PO_4, in distilled water and dilute to one liter. 1 ml = 100 µg phosphoric acid, H_3PO_4.

7.3 Sodium molybdate solution. Dissolve 25.0 g of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, in 10 N sulfuric acid and dilute to one liter with 10 N sulfuric acid.

7.4 Hydrazine sulfate solution. Dissolve 1.5 g of hydrazine sulfate, $N_2H_6SO_4$, in distilled water and dilute to one liter.

8. Procedure

8.1 Cleaning of glassware. Contamination of glassware by detergents should be guarded against, especially when small amounts of phosphorus are being determined. Many detergents contain phosphates. Glassware that may have been cleaned with such detergents should be boiled in 1:1 hydrochloric acid and rinsed carefully.

8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and shipping of samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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 be passed through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least ± 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank. With each batch of ten samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this a blank.

8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of filter tweezers.

8.4.2 Transfer the filter to a 125 ml Phillips beaker. Add 10 ml distilled water, cover with a watchglass and place on a steambath or equivalent for 10 minutes. Decant the water into a 50 ml volumetric flask and repeat with another 10 ml of distilled water. Rinse the inside of the beaker with an additional 5 ml of distilled water and transfer quantitatively to the 50 ml volumetric flask.

8.4.3 Pipet 5 ml of the sodium molybdate solution and 2 ml of the hydrazine sulfate solution into the volumetric flask. Dilute to the mark with distilled water and shake well.

8.4.4 Immerse the volumetric flask in a boiling water bath for 10 minutes. Remove and cool rapidly to room temperature.

8.4.5 Read the absorbance in a spectrophotometer at 830 nm against a reagent blank prepared in the same manner as the samples.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ± 5%.

For this validation study, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level has been used for the leaching studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then leached and analyzed as described in Section 8.4. The recovery values obtained were at least 99% and as such no correction factor has been used in the determination of the "true" values.

The percent recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}} \times 100$$

9. Calibration and Standards

9.1 Pipet into six 50 ml volumetric flasks 0, 0.25, 0.5, 1.0, 1.5, and 2.0 ml of the potassium dihydrogen sulfate solution.

9.2 Proceed as directed in Section 8.4.3

9.3 Construct a calibration curve by plotting absorbance against the equivalent concentration of phosphoric acid in µg/50 ml.

10. Calculations

10.1 Determine from the calibration curve (Section 9.3) the µg concentration of phosphoric acid present in each sample. No volume corrections are needed since both the samples and standards are in 50 ml total volume.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter
μg blank = μg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 P&CAM 216, Phosphoric Acid in Air.

11.3 M. Halmann, "Analytical Chemistry of Phosphorous Compounds", Vol. 37 of Chemical Analysis series by Elving and Kolthoff, John Wiley - Interscience, N.Y., 1972.

Tetrachloroethylene
(Perchloroethylene)

Analyte:	Tetrachloroethylene	Method No.:	S335
Matrix:	Air	Range:	655-2749 mg/cu m
OSHA Standard:	200 ppm (1355 mg/cu m)-Ceiling 100 ppm (680 mg/cu m)-T.W.A.	Precision ($\overline{CV}_T$):	0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 655-2749 mg/cu m at an atmospheric temperature and pressure of 25°C and 763.1 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 136-4065 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 58 mg of analyte when a test atmosphere containing 2749 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 113 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(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 as 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 655-2749 mg/cu m was 0.052. This value corresponds to a 70.5 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 8.8% 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.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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% OV-101 stationary phase on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Tetrachloroethylene, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 90°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3 liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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 Pump for Charcoal Tubes," September 15, 1972.

Trichloroethylene

Analyte:	Trichloroethylene	Method No.:	S336
Matrix:	Air	Range:	519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision ($\overline{CV}_T$):	0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The 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 as 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 519-2170 mg/cu m was 0.082. This value corresponds to an 88.2 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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% OV-101 stationary phase on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Trichloroethylene, reagent grade

7.3 Octane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Beryllium and Beryllium Compounds (as Be)

Analyte:	Beryllium	Method No.: S339
Matrix:	Air	Range: 2.68-11.84 µg/cu m
OSHA Standard:	5 µg/cu m - Ceiling 25 µg/cu m - Peak 2 µg/cu m - T.W.A.	Precision ($\overline{CV}_T$): 0.064
Procedure:	Filter collection, acid digestion, flameless atomic absorption	Validation Date: 9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric, sulfuric and perchloric acids to destroy the filter and any organic material, and the beryllium (including beryllium compounds) is then solubilized in dilute hydrochloric acid.

   1.3 The solutions of samples and standards are pipetted into the graphite furnace of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for beryllium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2.68-11.84 µg/cu m using a 40-liter sample at an atmospheric temperature and pressure of 23.5°C and 749 mm Hg. Under the conditions of sample size (40 liters), the working range of the method is estimated to be 1.5-15 µg/cu m.

   2.2 The sensitivity of this method using the 10-ml final solution volume is 3.5 ng of Be (0.35 ng/ml for a 1% absorption). The method may be expanded by adjusting the final volume.

3. Interferences

   There are no known interferences for the beryllium atomic absorption spectrophotometric assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.68-11.84 µg/cu m is 0.064. This value corresponds to a 0.32 ug/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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There is also no 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 quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of beryllium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.45 micrometer pore size.

6.3 Atomic absorption spectrophotometer having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region, a direct readout (or recorder output) proportional to absorbance units, a graphite furnace accessory and a background corrector accessory. The Perkin-Elmer 305B with HGA 2000 Graphite Furnace and Deuterium Background Corrector is an example. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scattering at the 234.9 nm wavelength.

6.3.1 Beryllium hollow cathode lamp.

6.3.2 High purity nitrogen.

6.3.3 Pressure reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for the nitrogen supply tank.

6.3.4 A suitable method for measuring peak heights or areas.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks and other convenient sizes for preparation of standards.

6.4.4 Eppendorf 25-µl pipettor with tips.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Beryllium metal, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 3 M hydrochloric acid (25 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water).

7.5 6 M hydrochloric acid.

7.6 Perchloric acid, 60% solution.

7.7 Concentrated sulfuric acid.

7.8 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of beryllium.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 To determine if the concentration of interest exceeds the ceiling OSHA standard, a sample size of 45 liters is recommended. Sample for 30 minutes at a flow rate of 1.5 liter per minute.

8.3.5 To determine if the concentration of interest exceeds the T.W.A. OSHA standard, a sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute for one hour.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

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 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 10 ml of concentrated nitric acid, 1 ml concentrated sulfuric acid, and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate just to dryness. Remove the beaker immediately.

8.4.3 Beryllium and beryllium compounds are soluble in dilute hydrochloric acid and no special precaution is needed to solubilize the beryllium.

8.4.4 Cool each beaker and dissolve residues in 10 ml 3 M hydrochloric acid. An attempt to make a quantitative transfer into a 10-ml volumetric flask is not recommended, and the dilution is carried out in the beaker. Therefore, the addition of 10 ml 3 M hydrochloric acid (Section 7.4) must be quantitative.

8.4.5 Pipette 25 µl of the solutions into the graphite tube using an automatic pipettor (such as the Eppendorf pipettor) with disposable plastic tips.

The instrumental parameters for the graphite furnace tube source power, background corrector and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying, charring and atomizing should be established in accord with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of beryllium during these steps.

To obtain reliable results, samples must be frequently alternated with standards which give responses close to those of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate and reinject a standard in duplicate,...etc.

Note: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak heights or areas, it must be rejected and replaced because results so obtained are not reliable.

8.4.6 Record the absorbance at 234.9 nm. Peak heights are used for this measurement if the response is rapid and the bases of the peaks are short and reproducible. If the bases of the peaks are broadened by the presence of contaminants, the areas of the absorption peaks will give more accurate measurements. Area measurements may be made by the use of a planimeter or an electronic integrator.

8.4.7 When very low concentrations are found in the sample, the sample can be dried and rediluted to a smaller volume of 5 ml and reinjected. Before following this procedure, caution must be taken to take a minimal amount of aliquots from the original sample.

8.4.8 Appropriate filter blanks must be analyzed in accordance with the total procedure.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the three levels (0.5X, 1X, and 2X the OSHA standard) using a stock solution of 112.5 mg beryllium in 20 ml of 6M hydrochloric acid and diluting to 250 ml with distilled water. Three sets of six filters are spiked with appropriate volumes of the stock solution. This corresponds to the amount of beryllium collected in a 45-liter sample at the 0.5X, 1X, and 2X levels respectively. Allow the filters to dry and place each filter in a cassette filter holder and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or,

$$A.M.R. = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 0.1 to 0.5 µg/10 ml from the 1000 µg/ml standard beryllium solution (Section 7.8). Make all standard solutions in 3 M hydrochloric acid and prepare fresh daily.

9.2 To determine the response, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbances during any given day.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbances versus the concentration of each standard in µg/10 ml, or if a smaller sample volume is used, make an appropriate calibration curve.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/10 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\mu g \text{ found (Section 10.2)}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in µg/cu m.

$$\mu g/\text{cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3) X 1000 liter/cu m}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Lead and Inorganic Lead Compounds

Analyte:	Lead and Inorganic Lead Compounds	Method No.:	S341
Matrix:	Air	Range:	0.128-0.399 mg/cu m
OSHA Standard:	0.2 mg/cu m	Precision ($\overline{CV}_T$):	0.072
Procedure:	Filter collection, nitric acid digestion, atomic absorption	Validation Date:	10/24/75

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are wet-ashed using nitric acid to destroy the organic matrix, and the lead (including lead compounds) is then solubilized in nitric acid.

   1.3 The solutions of samples and standards are analyzed by aspiration into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer using a hollow cathode lamp for lead.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.128-0.399 mg/cu m using a 180-liter sample at an atmospheric temperature and pressure of 22°C and 761 mm Hg. Under the conditions of sample size (180 liters), the working range of the method is estimated to be 0.028-1.0 mg/cu m.

   2.2 The sensitivity of the method using a 10-ml final solution volume is 2.3 microgram lead which under the condition of the sample size corresponds to 0.013 mg/cu m. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

3.1 No cationic interferences; however, phosphate, carbonate, iodide, fluoride, and acetate suppress absorbance significantly at concentrations ten times greater than lead. Addition of EDTA to the solution so that the sample solutions are 0.1 M with respect to EDTA will overcome this interference.

3.2 At 217 nm, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids, it is necessary to correct for non-atomic absorption by using a hydrogen continuim lamp.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.128-0.399 mg/cu m is 0.072. This value corresponds to a 0.014 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 was determined for the collecting medium, thus, 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 not 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 quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Lead hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate

6.4.1 100-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 3, 5, 7, 10 ml.

6.4.3 100-ml and 10-ml volumetric flasks.

6.5 Nalgene Bottles

6.5.1 Five 100-ml capacity Nalgene bottles for storing dilute lead standards.

6.5.2 One 1000-ml capacity Nalgene bottle for storing 100 ppm lead stock solution.

6.6 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute nitric acid (10 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water used for dilute lead standards).

7.4 Lead metal (granulated), reagent grade.

7.5 Lead Nitrate, reagent grade.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

8.3.9 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 100-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 2-3 ml of concentrated nitric acid to destroy the organic filter matrix. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Repeat this step twice. Cover each beaker with a watch glass and heat it on a high temperature hot plate (400°C) in a fume hood until a white ash appears. Using distilled water, carefully rinse the material on the bottom of the watch glass into the beaker, rinse sides of beaker, and allow the solution to evaporate to dryness.

8.4.3 Lead and its compounds are soluble in nitric acid, and no special precaution is needed to solubilize the lead.

8.4.4 Cool each beaker and dissolve residues in 1 ml concentrated nitric acid.

8.4.5 Quantitatively transfer the clear solutions to a 10-ml volumetric flask.

8.4.6 Rinse each beaker at least three times with 2-3 ml portions of distilled or deionized water and quantitatively transfer each rinse to the solution in the volumetric flask. Dilute all samples to 10 ml with distilled or deionized water.

8.4.7 Aspirat the solutions into an oxidizing air-acetylene flame and record the absorbance at 217 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume such as 5 or 10 ml before aspiration. In such a case, use no more acid solution in Section 8.4.4 than is necessary

to effect a quantitative transfer.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.8 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare a 100 ppm lead stock solution by dissolving 0.1 g lead metal in 100 ml concentrated nitric acid and dilute to 1 liter with deionized or distilled water.

9.2 From the 100 microgram/milliliter stock lead standard solution, prepare at least five working standards to cover the range from 10.0 to 100 micrograms/10 milliliters. Make all standard solutions in dilute nitric acid and store in 100-ml Nalgene bottles.

9.3 Aspirate each of the standard samples and record the absorptions.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram/10 milliliters. It is advisable to run standards both before and after the analysis on a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in μg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg/10 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Toluene

Analyte:	Toluene	Method No.:	S343
Matrix:	Air	Range:	145.5-582 ppm
OSHA Standard:	Ceiling - 300 ppm Peak - 500 ppm 8-hr. T.W.A. - 200 ppm	Precision ($\overline{CV}_T$):	0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	5/21/76

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 145.5-582 ppm at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 30-1000 ppm. 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 toluene and other substances in the air. The first section of the charcoal tube was found to hold 27.3 mg of toluene when a test atmosphere containing 2294 mg/cu m of toluene in air was sampled at 0.19 liter per minute for 62.6 minutes;

breakthrough was observed at this time, i.e., the concentration of toluene 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. Interferences

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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 145.5-582 ppm was 0.052. This value corresponds to a 15.6 ppm standard deviation at the OSHA ceiling 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 ceiling level using the overall sampling and analytical method were 3.8% 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 Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ± 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 (3-ft X 1/8-in. O.D. 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 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: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Toluene, reagent grade.

7.3 Hexane, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 nearer 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 At the ceiling concentration, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow rate of 0.20 liter per minute.

8.3.6 At the 8-hour time weighted average concentration, a sample size of 12 liters is recommenued. Sample at a flow rate of 0.20 liter per minute.

8.3.7 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.8 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.9 With each batch of ten samples submit one tube from the same lot of tubes 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 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.11 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. 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. 200°C injector temperature
5. 265°C manifold temperature (detector)
6. 155°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 evaporation of solvent

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 (100 mg) is measured into a 64 mm, 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 toluene containing 563.6 μg/μl is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample 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 2-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the OSHA ceiling 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. These standards are used to confirm the calibration of the gas chromatograph.

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/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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

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 CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Boron Oxide

Analyte:	Boron Oxide	Method No.:	S349
Matrix:	Air	Range:	7.8-27.7 mg/cu m
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.056
Procedure:	Filter collection, Gravimetric analysis	Validation Date:	2/27/76

1. Principle of the Method

1.1 A known volume of air is drawn through tared polyvinyl chloride filters to collect boron oxide.

1.2 The sample-containing filters are removed from the cassette and dried over a desiccant to constant weight using a suitable microbalance.

2. Range and Sensitivity

2.1 This method for boron oxide was validated, using carbon black as reference sample, over the range of 7.8-27.7 mg/cu m at an atmospheric temperature and pressure range of 18-25°C and 749-761 mm Hg, using a 100-liter sample. In order to prevent handling losses, a sample size of 50 liters is recommended. For this (60-liter) sample size, the working range of the method is estimated to be 6-30 mg/cu m.

2.2 Use of this method should be restricted to the collection of a total of not more than 2 mg of total particulate.

3. Interferences

3.1 The presence of any other particulate material in the air being sampled will be a positive interference since this is a gravimetric method.

3.2 Information on any other particulate materials present should be solicited. If the concentration of other particulates is known, then the boron oxide concentration can be determined by difference. If other particulate matter is known to be present and its concentration cannot be determined, then this method will not provide an accurate measure of the boron oxide concentration.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 7.8-27.7 mg/cu m was 0.056.

This value corresponds to a 0.84 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 100% was determined for the collection medium at the 2X level; thus, no bias was introduced in the sample collection step. Likewise, no significant bias in the analytical method is expected other than normal gravimetric errors. CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The analysis is simple but the method is non-specific and subject to interference due to presence of other particulates in the air being sampled.

6. Apparatus

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of boron oxide has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2), stainless steel support screen, and 37-mm, three-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Polyvinyl chloride membrane filter; 37-mm diameter, 2.0 micrometer pore size.

6.3 PetriSlide (Millipore) or plastic Petri dish - as filter holder for storage and weighing.

6.4 Desiccator

6.5 Microbalance capable of weighing to 10 micrograms. Particular care must be given to proper zeroing of the balance. The same balance should be used for weighing filters before and after sample collection.

7. Reagents

Drierite or any other suitable desiccant.

8. Procedure

8.1 Preparation of Filters - All filters must be dried and weighed prior to use.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect boron oxide, a personal sampler pump is used to pull air through a polyvinyl chloride membrane filter (Section 6.2). The filter holder is held together by tape or a shrinking band. If the filter holder does not fit snugly, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.0 liters per minute. After sampling, replace small plugs to seal filter cassettes.

8.2.2 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 If the outer surface of the cassette filter holder is heavily coated with dust, carefully swab the outer surface with a moist paper towel before opening the cassette so as to minimize sample contamination. Discard paper towel.

8.3.2 Open the cassette filter holder and carefully remove the polyvinyl chloride membrane filter from the holder and stainless steel screen with the aid of Millipore filter tweezers. Transfer filter to a PetriSlide.

8.3.3 Dry the filter to constant weight in a desiccator containing a desiccant. This takes about 12 hours.

8.3.4 Weigh the filter in a microbalance.

8.3.5 If other particulate matter is suspected to be present, appropriate analysis should be made to determine its composition (if necessary) and quantity. This value should be subtracted from the total particulate weight.

9. Calibration and Standards

This portion is not applicable. The only standardization required is that the microbalance be properly zeroed for all weighings and preferably the same microbalance should be used for weighing filters before and after sample collection.

10. Calculations

10.1 Record the tare weight, in µg, of the dry filter before sampling.

10.2 Record the weight, in µg, of the dried, sample-containing filter.

10.3 The difference between these two weights represents the µg sample.

10.4 Corrections for the blank must be made for each sample. (If found to be necessary, corrections should be made for other particulate matter.)

$$\mu g \text{ found} = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.5 Convert volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$Vs = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where

Vs = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = barometric pressure in mm Hg
T = ambient air temperature in degrees centigrade

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\mu\text{g found (Section 10.4)}}{Vs}$$

11. References

11.1 "Documentation of NIOSH Validation Tests," Contract No. CDC-99-74-45.

11.2 Carbon Black, No. S262, report prepared under NIOSH Contract No. CDC-99-74-45.

Chloroform

Analyte:	Chloroform	Method No.:	S351
Matrix:	Air	Range:	99.8-416 mg/cu m
OSHA Standard:	50 ppm (240 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 99.8-416 mg/cu m at an atmospheric temperature and pressure of 27°C and 760 mm Hg, using a 17-liter sample. Under the conditions of recommended sample size (15 liters) the probable useful range of this method is 25-750 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 11-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 22 mg of analyte when a test atmosphere containing 485 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. The breakthrough data are based on a prior experiment.

(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 as 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 99.8-416 mg/cu m is 0.057. This value corresponds to a 14 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 1.5% 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.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 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, graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Chloroform, spectroquality

7.3 Undecane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 of 15 liters is recommended. This can be accomplished by sampling for 15 minutes at a rate of 1.0 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 155°C injector temperature
5. 200°C manifold temperature (detector)
6. 75°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 15-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu\ m \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
MW	=	molecular weight
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 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.

Chromium, Metal and Insoluble Compounds

Analyte:	Chromium, Metal and Insoluble Compounds	Method No.:	S352
Matrix:	Air	Range:	0.493-1,830 mg/cu m
OSHA Standard:	1 mg/cu m	Precision ($\overline{CV}_T$):	0.076
Procedure:	Filter collection atomic absorption	Validation Date:	10/24/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose ester membrane filter to collect the analyte.

   1.2 Samples are ashed using hydrochloric and nitric acids to destroy the filter and other organic materials in the sample, and the chromium metal and insoluble chromium compounds are then dissolved in nitric acid.

   1.3 The solutions of samples and standards are aspirated into the reducing nitrous oxide-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for chromium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.493-1,830 mg/cu m using a 90-liter sample at an atmospheric temperature and pressure of 26°C and 761 mm Hg. Under the conditions of sample size (90 liters), the working range of the method is estimated to be 0.05-2.5 mg/cu m.

   2.2 The sensitivity of this method for a 90-liter air sample using the 20-ml final solution volume is 0.012 mg/cu m and should be adequate for most cases. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   3.1 Soluble chromium compounds will give a positive interference.

   3.2 Interferences from iron and nickel are minimized by using a reducing nitrous oxide-acetylene flame.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.493-1.830 mg/cu m is 0.076. This value corresponds to a 0.076 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of chromium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 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.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer. The instrument must be equipped with a nitrous oxide-acetylene burner head.

6.3.1 Chromium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used. Heating tape to warm nitrous oxide regulator during use.

6.4 Glassware, borosilicate:

6.4.1 100-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 3, 5, 7, 10 ml

6.4.3 100-ml volumetric flasks

6.4.4 20-ml graduated centrifuge tube

6.5 Nalgene Bottles

6.5.1 Five 100-ml Nalgene bottles to store working chromium AA standards

6.5.2 One 1000-ml Nalgene bottle to store stock chromium AA standard

6.6 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Dilute nitric acid (5 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water)

7.4 Hydrochloric acid, 6 M solution

7.5 Potassium dichromate, reagent grade

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 100-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample with 3 ml of 6 M hydrochloric acid to solubilize any chromium metal which may be present. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Repeat twice. Repeat this procedure again three times except use concentrated nitric acid instead of hydrochloric acid. After the digestion process is complete, cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a fume hood until a white ash appears. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse the sides of the beaker, and allow to evaporate to dryness.

8.4.3 Cool each beaker and dissolve residues in 1 ml concentrated nitric acid.

8.4.4 Quantitatively transfer the clear solutions to a 20-ml graduated centrifuge tube.

8.4.5 Rinse each beaker at least three times with 2-3 ml portions of distilled or deionized water and quantitatively transfer each rinsing to the solution in the centrifuge tube. Dilute all samples to 20 ml with distilled or deionized water.

8.4.6 Aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 357.9 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume such as 5 or 10 ml before aspiration. In such a case use no more acid solution in 8.4.3 than is necessary to effect a quantitative transfer.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare a 100 µg/ml chromium stock standard by dissolving 0.2829 g potassium dichromate in dilute nitric acid (Section 7.3) and diluting to 1 liter. Transfer to a 1-liter Nalgene bottle.

9.2 From the 100 µg/ml stock chromium standard, prepare at least 5 working standards to cover the range from 20 to 200 µg/20 ml. Make all standard solutions in dilute nitric acid and prepare fresh daily. Store in 100-ml Nalgene bottles. For samples having low Cr concentrations, standards should be prepared in the range of 1 to 10 µg/20 ml.

9.3 Aspirate each of the standard samples and record the absorptions.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in μg/20 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in μg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg/20 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

Dichloroethyl Ether

Analyte:	Dichloroethyl Ether	Method No.:	S357
Matrix:	Air	Range:	45-180 mg/cu m
OSHA Standard:	15 ppm (90 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.059
Procedure:	Adsorption on charcoal desorption with carbon disulfide GC	Validation Date:	5/21/76

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 45-180 mg/cu m at an atmospheric temperature and pressure of 24°C and 762 mm Hg, using a 15-liter sample. Under the conditions of sample size (15 liters), the probable useful range of this method is 10-270 mg/cu m. 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 dichloroethyl ether and other substances in the air. The first section of the charcoal tube was found to hold 16.7 mg of dichloroethyl ether when a test atmosphere containing 161 mg/cu m of dichloroethyl ether in air was sampled at 0.90 liter per minute for 115.3 minutes; breakthrough was observed at this time, i.e., the concentration of dichloroethyl

ether 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. Interferences

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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 45-180 mg/cu m was 0.059. This value corresponds to a 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 9.3% 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 Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ±5% at the recommended flow rate.

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. 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: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Dichloroethyl ether, reagent grade.

7.3 Hexane, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 nearer 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 15 liters is recommended. Sample at a flow rate of 1 liter per minute for 15 minutes. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples submit one tube from the same lot of tubes 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.

8.3.9 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. 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. 225°C injector temperature
5. 275°C manifold temperature (detector)
6. 135°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. 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 (100 mg) is measured into a 64 mm, 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 dichloroethyl ether in hexane (0.337 g/ml) is injected directly into the activated charcoal 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 15-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

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

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:

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.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

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.

Diisobutyl Ketone
(2,6-Dimethyl-4-heptanone)

Analyte:	Diisobutyl Ketone	Method No.:	S358
Matrix:	Air	Range:	145.5-582 mg/cu m
OSHA Standard:	50 ppm (290 mg/cu m)	Precision ($\overline{CV}_T$):	0.070
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	5/21/7(

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 145.5-582 mg/cu m at an atmospheric temperature and pressure of 23°C and 762 mm Hg, using a 12-liter sample. Under the conditions of sample size (12 liters), the probable useful range of this method is 30-1000 mg/cu m. 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 diisobutyl ketone and other substances in the air. The first section of the charcoal tube was found to hold 25 mg of diisobutyl ketone when a test atmosphere containing 582 mg/cu m of diisobutyl ketone in air was sampled at 0.20 liter per minute for 219 minutes; breakthrough was observed at this time,

i.e., the concentration of diisobutyl ketone 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. Interferences

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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 145.5-582 mg/cu m was 0.070. This value corresponds to a 20.3 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 1.4% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ± 5% at the recommended flow rate. (Reference No. 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. O.D. stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W DMCS.

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 Diisobutyl ketone, 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 nearer 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 12 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 $\pm$ 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 With each batch of ten samples submit one tube from the same lot of tubes 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.

8.3.9 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 (21 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 241°C manifold temperature (detector)
6. 71°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 evaporation of solvent

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-5.0 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 64 mm, 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 the analyte 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 12-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

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Soction 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.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

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 CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Dioxane

Analyte:	Dioxane	Method No.:	S360
Matrix:	Air	Range:	155 - 651 mg/cu m
OSHA Standard:	100 ppm (360 mg/cu m)	Precision ($\overline{CV}_T$):	0.054
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 155 - 651 mg/cu m at an atmospheric temperature and pressure of 21.5°C and 754 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters), the probable useful range of this method is 36 - 1080 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 11-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 26 mg of analyte when a test atmosphere containing 651 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 210 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. 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 as 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 155 - 651 mg/cu m was 0.054. This value corresponds to a 19 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 values obtained using the overall sampling and analytical method were 7.4% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 absorbing 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 absorbing 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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Dioxane, reagent grade

7.3 Decane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 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 of 10 liters is recommended. Sample at a rate 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 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (45 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 75°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10 liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. **Calculations**

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Isophorone

Analyte:	Isophorone	Method No.:	S367
Matrix:	Air	Range:	67.5-283 mg/cu m
OSHA Standard:	25 ppm (140 mg/cu m)	Precision ($\overline{CV}_T$):	0.058
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	5/21/76

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 67.5-283 mg/cu m at an atmospheric temperature and pressure of 23°C and 764 mm Hg, using a 12-liter sample. Under the conditions of sample size (12 liters) the probable useful range of this method is 2-400 mg/cu m. 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 isophorone and other substances in the air. The first section of the charcoal tube was found to hold at least 13 mg of isophorone when a test atmosphere containing 283 mg/cu m of isophorone in air was sampled at 0.19 liter per minute for 240 minutes; breakthrough was not observed at this time since no isophorone was detected in the backup section of the

charcoal tube. (The charcoal tube consists of two sections of activated petroleum based 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. Interferences

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 interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 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 67.5-283 mg/cu m was 0.058. This value corresponds to an 8 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% 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 Section 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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

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 ± 5% at the recommended flow rate. (Reference No. 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 petroleum-based charcoal (Lot 104, supplied by SKC, Inc. or equivalent*) separated by a 2-mm portion of urethane foam. 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. I.D. stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W DMCS.

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.

*Lot 104 is a petroleum-based charcoal which is less active than Lot 105. The Lot 105 charcoal is prepared from coconut shells. A highly activated charcoal such as Lot 105 should not be used to collect isophorone.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Isophorone, reagent grade.

7.3 Hexane, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 nearer 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 12 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 With each batch of ten samples submit one tube from the same lot of tubes 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.

8.3.9 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. 255°C injector temperature
5. 250°C manifold temperature (detector)
6. 167°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 evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility

of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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 64 mm, 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 a hexane solution of isophorone containing 424.6 μg/μl is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 12-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

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

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 this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to 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.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

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, 1973.

Isopropyl Ether

Analyte:	Isopropyl Ether	Method No.:	S368
Matrix:	Air	Range:	992-4260 mg/cu m
OSHA Standard:	500 ppm (2100 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	5/21/76

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 992-4260 mg/cu m at an atmospheric temperature and pressure of 29°C and 764 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 200-6000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 18-mg sample. 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 analyte and other substances in the air. The first section of the charcoal tube was found to hold 21.9 mg of analyte when a test atmosphere containing 4260 mg/cu m of analyte in air was sampled at 0.198 liter per minute for 26 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent. (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 as 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 992-4260 mg/cu m was 0.056. This value corresponds to a 118 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 2% 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.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 80/100 mesh Chromosorb WAW-DMCS.

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 conveniert sizes for making standards.

6.8 Pipets: 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. **Reagents**

7.1 Chromatographic quality carbon disulfide.

7.2 Isopropyl ether, reagent grade.

7.3 Octane, or other suitable internal standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 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 backup 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 of 3 liters is recommended. Sample at a rate of 0.05 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. Submit one blank for every 10 samples.

8.3.9 Capped charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 150°C injector temperature
5. 220°C manifold temperature (detector)
6. 80°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5, 1 and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are 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 amount of analyte into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$\text{D.E.} = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

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 per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2S the standard. The analyte concentration in mg per ml is plotted versus the ratio of the area of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (Liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Magnesium Oxide Fume

Analyte:	Magnesium Oxide	Method No.:	S369
Matrix:	Air	Range:	7.48-28.6 mg/cu m
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.062
Procedure:	Filter collection, Atomic absorption	Validation Date:	10/24/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric acid to destroy the filter and other organic materials in the sample, and the magnesium is then solubilized in nitric acid.

   1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for magnesium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 7.48-28.6 mg/cu m using a 150-liter sample at atmospheric temperature and pressure of 23°C and 764 mm Hg. Under the conditions of sample size (150 liters), the working range of the method is estimated to be 1-55 mg/cu m.

   2.2 The sensitivity of this method for a 150-liter air sample using the 100-ml final solution volume is 0.33 mg/cu m magnesium. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response. The sensitivity may be extended by using the resonance line at 285.2 nm.

3. Interferences

   3.1 Any magnesium compound which is collected on the cellulose ester membrane filter will cause a positive interference.

   3.2 Si, Al, and Cu (at high concentrations) may interfere with the method. These interferences can be eliminated by adding 0.1-1.0% of La to 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 7.48-28.6 mg/cu m is 0.062. This value corresponds to a 0.93 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 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of magnesium oxide content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm three-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Magnesium hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 100-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 3, 5, 7, 10, 15, 20 ml.

6.4.3 100-ml volumetric flasks.

6.4.4 250-ml volumetric flasks.

6.5 Nalgene Bottles

6.5.1 Five 100-ml capacity Nalgene bottles for working atomic absorption standards.

6.5.2 One 1000-ml capacity Nalgene bottle for stock atomic absorption standard.

6.6 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Double distilled water

7.2 Concentrated nitric acid

7.3 Dilute nitric ac (10 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water)

7.4 Magnesium metal for preparation of AA standards, or commercially prepared aqueous stock standards (1000 micrograms/ml)

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 150 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm 5\%$.

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 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters 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.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 100-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 3 ml of concentrated nitric acid to destroy the organic filter matrix. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Repeat this step twice. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a fume hood until a white ash appears. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate to dryness.

8.4.3 Cool each beaker and dissolve residues in 10 ml concentrated nitric acid.

8.4.4 Quantitatively transfer the clear solutions to a 100-ml volumetric flask.

8.4.5 Rinse each beaker at least three times with 2-3 ml portions of distilled water or deionized water and quantitatively transfer each rinse to the solution in the volumetric flask. Dilute all samples to 100 ml with distilled or deionized water.

8.4.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 202.5 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume such as 5 or 10 ml before aspiration. In such a case, use no more acid solution in 8.4.3 than is necessary to effect a quantitative transfer. If greater sensitivity is needed, the analytical wavelength at 285.2 nm may be used.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.7 For samples with concentration levels in excess of 2000 micrograms/100 ml (20 ppm Mg is the high limit of the linear working range of the standard curve obtained at 202.5 nm) take an aliquot of the remaining sample and dilute to 100 ml with 1:10 nitric acid. Choose the aliquot such that when it is diluted to 100 ml, the dilution ratio brings the concentration of the sample within the linear working range of the calibration curve.

8.4.8 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare a 100 micrograms/ml magnesium stock standard by dissolving 100 mg magnesium metal in 100 ml concentrated nitric acid and diluting to 1000 ml. Transfer to a 1-liter Nalgene bottle.

9.2 From the 100 micrograms/ml stock magnesium standard solution, prepare at least seven working standards to cover the linear range of the standard curve of 100 to 2000 micrograms/100 ml. Make all standard solutions in dilute nitric acid and prepare fresh each day and store in 100-ml Nalgene bottles.

9.3 Aspirate each of the standard samples and record the absorptions.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in micrograms/100 ml. It is advisable to run standards both before and after the analysis on a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/100 ml.

10.2 For concentrated samples which require dilution after initial analysis to bring them within the linear range of the standard curve (as in 8.4.7), apply the appropriate dilution factor to obtain the correct weight of magnesium in the sample.

10.3 Corrections for the blank must be made for each sample.

$$\text{microgram} = \text{microgram sample} - \text{microgram blank}$$

where:

$$\text{microgram sample} = \text{microgram found in sample filter}$$

$$\text{microgram blank} = \text{microgram found in blank filter}$$

10.4 Calculate the micrograms of magnesium oxide by multiplying the micrograms magnesium found (Section 10.3) by 1.66, which is a conversion factor to convert micrograms magnesium to micrograms magnesium oxide.

10.5 The concentration of the analyte in the air sample can be expressed in mg/cu m (microgram/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{microgram (Section 10.4)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Malathion

Analyte:	Malathion	Method No.:	S370
Matrix:	Air	Range:	8.0-35 mg/cu m
OSHA Standard:	15 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.063
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date:	9/30/76

1. Principle of the Method

   1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter containing malathion.

   1.2 Malathion is extracted from the filter with iso-octane, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 7.96-35.2 mg/cu m at an atmospheric temperature of 20°C and atmospheric pressure of 760 mm Hg, using a 100-liter sample.

   2.2 The upper limit of the range of the method depends on the capacity of the glass fiber filter. If higher concentrations than those tested are to be sampled, smaller volumes should be used.

3. Interferences

   3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

   3.2 Any compound that has the same retention time as malathion at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 7.96-35.2 mg/cu m was 0.063. This value corresponds to a standard deviation of 0.9 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter glass fiber filter (Gelman Type AE or equivalent) and a polystyrene 37-mm two-piece cassette filter holder. The filter is held in the two-piece filter holder supported by a stainless steel support screen. The filter must be free of organic binders. Filter holders made of Tenite should not be used.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined within 5% at the recommended flow rate.

6.3 Manometer.

6.4 Thermometer.

6.5 Scintillation vials: Within one hour after sample has been collected, the filter is transferred to a clean scintillation vial (20 ml) for shipping. The vial caps should be lined with Teflon for proper seal.

6.6 Gas chromatograph equipped with a flame photometric detector with a phosphorous filter.

6.7 Column (6-ft long X ¼-in O.D. glass) packed with 1.5% OV-17 and 1.95% OV-210 on 80/100 mesh Gas Chrom Q.

6.8 An electronic integrator or some other suitable method for measuring peak areas.

6.9 Tweezers.

6.10 Microliter syringes: 10-microliter.

6.11 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.12 Pipets: Convenient sizes for preparing standard solutions, and 15-ml pipets for measuring the collection medium.

7. Reagents

7.1 Malathion, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Nitrogen, purified.

7.4 Hydrogen, prepurified.

7.5 Oxygen, purified.

7.6 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a stainless steel support screen.

8.3.2 Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and record ambient temperature and pressure, sample flow rate, and collection time. If pressure reading is not available, record the elevation.

8.3.7 Remove the glass fiber filter from the cassette filter holder within one hour of sampling and place it in a clean scintillation vial. Care must be taken to handle the filter with clean tweezers.

8.3.8 Pipet 15 ml of iso-octane into each screw cap bottle and mark the liquid level with a china marker.

8.3.9 Record the sample identity and all relevant sampling data.

8.3.10 With each batch of ten samples, submit one filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

8.3.11 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.3.12 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 collected samples.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately.

8.4.2 Swirl the contents in each bottle. Adjust the liquid level of iso-octane if necessary.

8.4.3 Appropriate filter blanks must be analyzed at the same time as the samples.

8.4.4 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 60 ml/min nitrogen carrier gas flow
2. 125 ml/min hydrogen gas flow to detector
3. 20 ml/min oxygen gas flow to detector
4. 35 ml/min air flow to detector
5. 185°C column temperature
6. 200°C detector temperature
7. 240°C injector temperature

8.4.5 Injection. The first step in the analysis is to inject the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, a solvent flush injection technique should be used. A 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, 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 before 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.

Since a 5-microliter aliquot is likely to cause the flame to blow out, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.4), it was found that 30 seconds was adequate to elute the solvent.

8.4.6 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. 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/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of day-to-day variations and variations during the same day of the flame photometric detector response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter

mg blank = mg found in blank filter

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 If air samples are taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \text{ (Section 10.3)} \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air (liters) at 25°C and 760 mm Hg

V = volume of air sampled

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

10.5 The concentration of malathion in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2) x 1000 (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.2 Backup Data Report for Malathion, prepared under NIOSH Contract No. 210-76-0123.

Methyl Bromide

Analyte:	**Methyl Bromide**	**Method No.:**	**S372**
Matrix:	**Air**	**Range:**	**35-150 mg/cu m**
OSHA Standard:	**20 ppm (80 mg/cu m)-Ceiling**	**Precision ($\overline{CV}_T$):**	**0.103**
Procedure:	**Adsorption on charcoal, desorption with carbon disulfide, GC**	**Validation Date:**	**6/6/75**

1. Principle of the Method

1.1 A known volume of air is drawn through a large charcoal tube to trap the organic vapors present. The sampling tube consists of two separate tubes--a front adsorbing tube and a backup tube; this sampling arrangement is necessary to prevent sample migration effects upon storage.

1.2 The charcoal in each tube is transferred to a 5-ml, screw-capped 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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 35-150 mg/cu m at an atmospheric temperature and pressure of 24.2°C and 767 mm Hg, using an 11-liter sample. Under the conditions of recommended sample size (11 liters) the probable useful range of this method is 20-250 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the front charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The front adsorbing charcoal tube was found to hold 2.9 mg of analyte when a test atmosphere containing 161 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 94 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube series consists of two separate large tubes: the first tube contains 400 mg of charcoal and the second tube used as the backup tube contains 200 mg of charcoal. The charcoal is held in place by glass wool plugs at the tube ends. 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 as 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 35-150 mg/cu m is 0.103. This value corresponds to an 8.2 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 4.5% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can

be eliminated by altering chromatographic conditions. The 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 charcoal tube exceeds 25% of that found on the front tube, 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 ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: The sampling tube series consists of two separate large charcoal tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with an 8-mm O.D. and a 6-mm I.D. Each tube contains the appropriate amount of 20/40 mesh activated charcoal (petroleum-based). The front tube contains 400 mg of charcoal; the backup tube 200 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

This tube series can be prepared by modifying commercially available large charcoal tubes as follows. For the front tube--break off exit end of a large tube and using pointed tweezers remove glass wool plug and the backup charcoal section; push in snugly remaining plug and charcoal to minimize channelling. For the backup tube--similarly break off inlet end of a second large tube and remove retaining plug and the front charcoal section; again push together remaining plug and charcoal. The front tube is connected to the backup tube with a minimal piece of tygon or rubber tubing.

Note that this sampling tube scheme is necessary to minimize observed sample migration effects upon storage.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Five-milliliter sample containers with Teflon-lined screw caps, such as the 5-ml vials distributed by SKC, Inc., Pittsburgh, Pa.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 2.0 ml, graduated or delivery.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methyl bromide, 99.5%

7.3 Decane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 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 sampling tube series in the line assembled as noted in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube (3 mm). Prepare and assemble as described in Section 6.2. Connect the front 400-mg tube to the 200-mg backup tube with a short piece of tubing.

8.3.2 The tube containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube series should be placed in a vertical direction during sampling to minimize channelling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

8.3.5 A maximum sample size of 11 liters is recommended. This can be accomplished by sampling for 15 minutes at a rate of 0.75 liter per minute, or by sampling for 11 minutes at 1 liter per minute. 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 front charcoal tube should be separated from the backup tube immediately after sampling. Both tubes must be labelled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 One set of tubes prepared as described in Section 6.2 should be handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through these tubes. These tubes should be labelled as the blank.

8.3.9 Capped charcoal 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 and broken open. The glass wool is removed and discarded. The charcoal in the front tube is transferred to a 5-ml sample container with Teflon-lined screw cap. Similarly, the charcoal in the backup tube is transferred to another container. These two charcoal tubes are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 2.0 ml of carbon disulfide is pipetted into each sample container. Cap the

vials tightly immediately after the addition of carbon disulfide. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, carefully transfer portions of the desorbed sample solution to the automatic sample injector vials and cap tightly. For the internal standard method, desorb using 2.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 155°C injector temperature
5. 200°C manifold temperature (detector)
6. 65°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 blowback 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 can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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 front tube (400 mg) is measured into a 10-cm long, 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 a concentrated solution of the analyte in carbon disulfide* is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. Alternatively, the 5-ml tubes or vials used for desorption may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in an 11-liter sample at the selected level. The tubes are 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 the methyl bromide solution in carbon disulfide into 2.0 ml of carbon disulfide with the same syringe used in the preparation of the spiked samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the

*This solution of methyl bromide in carbon disulfide can be prepared by bubbling methyl bromide gas into carbon disulfide in a fritted glass bubbler. The methyl bromide concentration of the solution is determined by comparison with gas standards.

weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 2.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The calibrated solution of methyl bromide in carbon disulfide as described in Section 8.5.2 can be used to prepare calibration solutions. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 2.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per 2.0 ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

mg = mg sample - mg blank

where:

mg sample = mg found in front (400-mg) sample tube
mg blank = mg found in front (400-mg) blank tube

A similar procedure is followed for the backup tube.

10.3 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Molybdenum, Insoluble Compounds

Analyte:	Molybdenum	Method No.:	S376
Matrix:	Air	Range:	6.3-30.6 mg/cu m
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.056
Procedure:	Filter collection, Acid digestion, Atomic absorption	Validation Date:	10/24/75

1. Principle of the Method

1.1 Samples collected on filters are treated with nitric/perchloric acid or base/nitric acid depending on solubility characteristics, i.e., acid soluble vs. base soluble. This solubility test is performed on a bulk sample prior to sample analysis. After digestion, sulfuric acid is added to dissolve any precipitate formed and aluminum is added to enhance the signal and to control probable aluminum interference.

1.2 The solutions of samples and standards are aspirated into the nitrous oxide-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for molybdenum is used to provide a characteristic molybdenum line at 313.3 nm.

1.3 The absorption at the 313.3 nm line is proportional to the molybdenum concentration in the aspirated sample.

2. Range and Sensitivity

2.1 This method was validated over the range of 6.3-30.6 mg/cu m at an atmospheric temperature and pressure of 19°C and 767 mm Hg, using a 90-liter sample. Under the conditions of sample size (90 liters), the linear working range of the method is estimated to be 2-50 mg/cu m using the solution volumes and experimental conditions specified.

2.2 The method may be extended to higher concentrations by further dilution of the sample and also to lower concentrations by collecting a larger sample volume.

3. Interferences

3.1 The water soluble molybdenum compounds (OSHA standard = 5 mg/cu m) will give a positive interference.

3.2 The interferences as variable enhancement which would result from the presence of small amount of aluminum and traces of acidity are alleviated by adding aluminum at a concentration of 400 µg/ml.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method for acid-soluble molybdenum compounds in the range of 6.3-30.6 mg/cu m was 0.056. This value corresponds to a standard deviation of 0.84 mg/cu m at the OSHA standard. The statistical data are based on the analysis of analytical samples and collected air samples treated according to the procedure for acid-soluble molybdenum compounds. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3. Limited data based on the analysis of MoO_3 according to the procedure for base soluble molybdenum compounds gave a CV_1 value of 0.049.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method--the average recovery from the filters for analytical samples prepared with sodium molybdate was 100.3% and 103.5% for analytical samples prepared with MoO_3. These samples were analyzed according to the procedures for acid-soluble molybdenum compounds. Similarly, a limited number of analytical samples prepared with MoO_3 and analyzed according to the procedure for base-soluble molybdenum compounds, gave average recoveries of 98.5%. Thus, CV_T is a measure of both accuracy and precision.

5. Advantages and Disadvantages of the Method

5.1 The method is simple and accurate.

5.2 A bulk sample is necessary in order to determine the sample solubility characteristics and the appropriate analysis procedure.

6. Apparatus

6.1 Sampling Equipment - the sampling unit for the collection of personal air samples for the determination of metal content has the following components;

6.1.1 The filter units, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Manometer

6.1.4 Thermometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultra-violet region. The instrument must have the necessary nitrous oxide-acetylene burner head.

6.3.1 Molybdenum hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used. Wrap the second stage of the nitrous oxide regulator and the connecting hose with heating tape, where the temperature is controlled by a rheostat, in order to prevent freeze-up of the line.

6.4 Glassware, borosilicate

6.4.1 125 ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 50 ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Perchloric acid, 70%

7.3 Concentrated nitric acid

7.4 **Concentrated sulfuric acid**

7.5 **Sodium hydroxide solution, 2 N and 6 N**

7.6 **Commercially prepared aqueous aluminum solution, 10,000 µg/ml**

7.7 **Commercially prepared aqueous standard molybdenum stock solutions, 1000 µg/ml**

8. Procedure

8.1 Cleaning of Equipment

8.1.1 **Before use all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemical.**

8.1.2 **After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.**

8.2 Sampling Requirements and Shipping of Samples

8.2.1 **To collect the analyte aerosol a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.2). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.**

8.2.2 **Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as blank.**

8.2.3 **Bulk samples. In order to determine the solubility characteristics of the insoluble molybdenum compound a portion of the bulk sample must be submitted to the laboratory to test solubility. A small portion of the bulk sample (ca. 0.10 g) should be treated with a few ml (ca. 10 ml) of concentrated acid and heated gently on a hot plate if necessary. Another 0.10 g portion should be treated with 10 ml of 6 N NaOH. Based on the results of these solubility tests, the samples should be processed using the appropriate sample treatment procedure described in Section 8.3.2. If no conclusive**

visual results are obtained, the acidic and basic solutions should be analyzed for molybdenum in accordance with the method described in the preparation of calibration solutions. Reference standard used must be in the same matrix as the bulk sample being analyzed.

8.2.4 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker. Since some solids may have transferred from the filter to the sides of the cassette during the shipping and handling, if deemed necessary, carefully wash the interior of the cassette with a few ml of distilled water (in a fine stream) and transfer the washings to the same 125-ml Phillips beaker.

8.3.2 Sample processing, wet ashing and digestion. Use one of the two methods described depending on the solubility of the bulk sample.

1. For acid-soluble molybdenum compounds. (This is the preferred method whenever feasible.) To destroy the organic filter matrix, treat the sample with 2 ml of concentrated nitric acid. Cover the beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process once more using 2 ml of concentrated nitric acid. Cool beaker and contents and add 3 ml of HNO_3-$HClO_4$ mixture and continue evaporating to fumes to effect complete digestion of sample. Do not allow to evaporate to dryness at any point. Allow solution to cool.

   A precipitate may be observed after the digestion process. Add 5 drops of concentrated sulfuric acid and heat gently until precipitate is dissolved. An ultrasonic agitator may be used to hasten dissolution process. Allow to cool.

2. For base-soluble molybdenum compounds. (Use this procedure only when necessary and exercise due caution because an explosive mixture may be formed.) Add 5 ml of 2 N sodium hydroxide and heat gently with occasional swirling to solubilize the molybdenum. The solution may be heated till the volume decreases to 3 ml. Cool

in an ice-bath and slowly add 5 ml of concentrated nitric acid. Heat cautiously, with occasional swirling, to white fumes and treat with another 3-ml portion of nitric acid and heat again to complete the sample digestion. A moderate amount of white crystals, which is most likely sodium nitrate, are formed; however, tests indicate that these crystals redissolve during the final sample dilution. Allow the solution to cool and add 5 drops of concentrated sulfuric acid. Heat gently again for about 5 minutes and allow to cool.

8.3.3 Add 10 ml of distilled water and quantitatively transfer to a 50-ml volumetric flask.

8.3.4 Rinse Phillips beaker at least twice with 10 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.5 Add 2 ml of aluminum solution containing 10,000 µg/ml.

8.3.6 Dilute to 50 ml with distilled water.

8.3.7 Aspirate the solutions into a nitrous oxide--acetylene flame and record the absorbance at 313.3 nm. The absorbance is proportional to the molybdenum concentration. It is recommended that the samples be frequently alternated with standards which give absorbances close to that of the sample in order to minimize the observed variations in flame characteristics and responses of the nitrous oxide--acetylene flame due to the gradual accumulation of carbon deposits around the burner slot. These carbon deposits should be scraped off regularly.

NOTE: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

8.4.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter by digestion and analyzed as described in Section 8.3. Duplicate determinations should agree within ±5%.

For the studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) were spiked accordingly. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filter samples were then digested and analyzed as described in Section 8.3. The recovery values obtained were 100% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 From the 1000 µg/ml stock standard solution, prepare at least six working standards to cover the concentration range from 500-5000 µg/50 ml. It is convenient to express the concentration in µg/50 ml because all samples are diluted to this total volume. All standard solutions are acidified with 5 drops of sulfuric acid; solutions should be prepared fresh daily.

9.2 For the acid soluble molybdenum compounds, proceed as in Section 8.3.5 to 8.3.7. For the base-soluble molybdenum compound, add 850 mg sodium nitrate and proceed as in Section 8.3.5 to 8.3.7.

9.3 The appropriate calibration standards are alternately analyzed with the samples to determine the appropriate calibration or response factor. This practice will minimize the effect of observed fluctuations or variations in absorbance readings during any given day.

10. Calculations

10.1 Determine the weight, in µg, corresponding to the absorbance of the sample by using the appropriate calibration or response factor determined from the response of the standards. No volume corrections are needed, because the standard curve is based on µg per 50 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 Convert volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$Vs = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where:

Vs = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = barometeric pressure in mm Hg
T = ambient air temperature in degree centigrade

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.3)}}{\text{Vs (Section 10.4)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn. 1971.

11.2 Methods for Emission Spectrophotometry Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Analyte:	Octane	Method No.: S378
Matrix:	Air	Range: 1050 - 4403 mg/cu m
OSHA Standard:	500 ppm (2350 mg/cu m	Precision ($\overline{CV}_T$): 0.060
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 3/14/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1050 - 4403 mg/cu m at an atmospheric temperature and pressure of 20°C and 758 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters), the probable useful range of this method is 235 - 7050 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 28 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 30 mg of analyte when a test atmosphere containing 4612 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 34 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The 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 as 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 1050 - 4403 mg/cu m was 0.060. This value corresponds to a 141 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 values obtained using the overall sampling and analytical method were 5.2% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 absorbing 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 absorbing 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 (20-ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Octane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 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 of 4 liters is recommended. Sample at a rate 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 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Pentane

Analyte:	Pentane	Method No.:	S379
Matrix:	Air	Range:	1476-6190 mg/cu m
OSHA Standard:	1000 ppm (2950 mg/cu)	Precision ($\overline{CV}_T$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

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 from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1476-6190 mg/cu m at an atmospheric temperature and pressure of 24°C and 769 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 300-8850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 18-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 18 mg of analyte when a test atmosphere containing 5640 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 16.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(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 as 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 1476-6190 mg/cu m was 0.055. This value corresponds to a 160 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 values obtained using the overall sampling and analytical method were 9.7% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 absorbing 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 absorbing 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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Pentane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 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 of 2 liters is recommended. Sample at a rate of 0.05 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°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 technique.

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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 2-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 desorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Petroleum Distillate

Analyte:	Petroleum Distillate	Method No.:	S380
Matrix:	Air	Range:	937-3930 mg/cu m
OSHA Standard:	500 ppm (2000 mg/cu m)	Precision ($\overline{CV}_T$):	0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

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 total area of the resulting peaks is determined and compared with corresponding areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 937-3930 mg/cu m at an atmospheric temperature and pressure of 24°C and 755 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters) the probable useful range of this method is 200-6000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 24-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 24.6 mg of analyte when a test atmosphere containing 3930 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 33 minutes; breakthrough was observed at this time. i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(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 When analyzing solvent mixtures such as this analyte, search for differences in gas chromatographic patterns between field samples and bulk or head space samples as evidence of an interference. It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 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 937-3930 mg/cu m was 0.052. This value corresponds to a 104 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 values obtained using the overall sampling and analytical method were 4.2% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 absorbing 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 absorbing 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% OV-101 on 100/120 mesh Supelcoport.

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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Petroleum Distillate (Boiling range: 120-147°C)

7.3 Decane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 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 of 4 liters is recommended. Sample at a rate 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 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 charcoal 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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 85°C column temperature

Note: The GC conditions have been chosen such that the analyte-related peaks elute as a cluster of unresolved peaks. Watch for distinctive patterns in searching for interferences and adjust GC conditions accordingly.

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 technique.

8.4.5 Measurement of area. The total area of the 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 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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4-liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

Bulk samples of the analyte should be used for the calibration.

It is convenient to express concentration of standards in terms of mg per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus total area of relevant peaks.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte peaks to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Stoddard Solvent

Analyte:	Stoddard Solvent	Method No.:	S382
Matrix:	Air	Range:	1417-5940 mg/cu m
OSHA Standard:	500 ppm (2950 mg/cu m)	Precision ($\overline{CV}_T$):	0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

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 total area of the resulting peaks is determined and compared with corresponding areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1417-5940 mg/cu m at an atmospheric temperature and pressure of 24°C and 749 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 295-8850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 26.6-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 26.3 mg of analyte when a test atmosphere containing 6026 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 23 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(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 When analyzing solvent mixtures such as this analyte, search for differences in gas chromatographic patterns between field samples and bulk or head space samples as evidence of an interference. It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 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 1417-5940 mg/cu m was 0.052. This value corresponds to a 153.4 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 values obtained using the overall sampling and analytical method were 4.7% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The 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 ±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 absorbing 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 absorbing 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 (6-ft x 1/8-in stainless steel) packed with 1.5% OV-101 on 100/120 mesh 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 type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Stoddard Solvent (Boiling range: 159-176 °C)

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 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 of 3 liters is recommended. Sample at a rate 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 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 charcoal 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 4-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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 75°C column temperature

Note: The GC conditions have been chosen such that the analyte-related peaks elute as a cluster of unresolved peaks. Watch for distinctive patterns in searching for interferences and adjust GC conditions accordingly.

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 technique.

8.4.5 Measurement of area. The total area of the 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 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 the analyte is injected directly into the activated charcoal 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.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3 liter sample at the selected level. The tubes are 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.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

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

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

Bulk samples of the analyte should be used for the calibration.

It is convenient to express concentration of standards in terms of mg per 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus total area of relevant peaks.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte peaks to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 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:

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 amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times \text{1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 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.

Titanium Dioxide

Analyte:	**Titanium Dioxide**	**Method No.:**	S385
Matrix:	**Air**	Range:	8.1-29.5 mg/cu m
OSHA Standard:	**15 mg/cu m**	**Precision ($\overline{CV}_T$):**	**0.112**
Procedure:	Filter collection Acid digestion Atomic absorption	Validation Date:	10/24/75

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix.

1.2 The titanium dioxide is solubilized by further heating with sulfuric acid and ammonium sulfate.

1.3 The solutions of samples and standards are aspirated into the nitrous oxide-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for titanium is used to provide a characteristic titanium line at 364.3 nm. The absorbance is proportional to the titanium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 8.1-29.5 mg/cu m at an atmospheric temperature and pressure of 23°C and 767 mm H_g, using a 100-liter sample. Under the conditions of sample size (100 liters), the linear working range of the method is estimated to be 2-35 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

Ammonium fluoride strongly enhances the titanium absorbance (Reference 11.4). If fluorides are known to be present, an excess of ammonium fluoride should be deliberately added to the sample solutions and standard solutions.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.1-29.5 mg/cu m was 0.112 This value corresponds to a 1.7 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 11.3.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the filters was 97%. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The method is simple.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for a nitrous oxide-acetylene flame.

6.3.1 Titanium hollow cathode lamp

6.3.2 Nitrous oxide

6.3.3 Fuel: purified acetylene

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used

6.4 Glassware, borosilicate: Use glassware only if fluorides are absent.

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10-ml and other convenient sizes for making standards.

6.4.3 50-ml volumetric flasks

6.5 Adjustable thermostatically-controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Nitric acid, 0.1N

7.4 Concentrated sulfuric acid

7.5 Sulfuric acid/ammonium sulfate mixture. Dissolve 40 g of ammonium sulfate in 100 ml of sulfuric acid.

7.6 Aqueous standard titanium stock solution, 500 µg/ml as titanium. Dissolve 0.4170 g of dried, analytical reagent grade titanium dioxide in 25 ml of the sulfuric acid/ammonium sulfate mixture. Dilute to 500 ml with water in a volumetric flask. A commercially available titanium stock solution (1000 µg/ml) may also be used.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect titanium dioxide dust, a personal sampler pump is used to pull air through a cellulose ester

membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.2 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker. Rinse the inner portion of the cassette holder with distilled water and transfer rinsings to Phillips beaker.

NOTE: If the outer surface of the cassette filter holder is heavily coated with dust, carefully swab the outer surface with moistened paper towel before opening the cassette so as to minimize sample contamination. Discard the paper towel.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 3 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process once more using 3 ml of concentrated nitric acid. Do not allow the solution to evaporate to dryness. Cool solution.

8.3.3 Titanium dioxide dissolution. To ensure complete dissolution of titanium dioxide, add 8 ml of the sulfuric acid/ammonium sulfate mixture and continue heating on a high temperature hot plate (400°C) until all the remaining solids completely dissolve. This heating cycle will require approximately 60 minutes. To avoid "bumping" during the dissolution process, add a couple of glass

beads. Do not allow the solution to evaporate to dryness at any point. If fluorides are present, some loss of titanium due to formation of titanium tetrafluoride may occur.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 50-ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 5 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute to volume.

NOTE: If fluorides are known to be present, add 5 ml of 1N ammonium fluoride before diluting to volume.

8.3.7 Aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 364.3 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.6 than is necessary to effect a quantitative transfer.

NOTE: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

8.4.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within +5%.

For this validation study, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly by adding weighed amounts of titanium dioxide. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 97%.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

9. Calibration and Standards

9.1 From the standard titanium stock solution, prepare at least six working standards to cover the titanium concentration range from 0.2 to 3.0 mg/ml. Add 8 ml of the sulfuric acid/ammonium sulfate mixture to each of these working standard solutions and dilute to 50 ml with 0.1N nitric acid. Prepare these working standards fresh daily.

9.2 Proceed as in Section 8.3.7.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in mg/50 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight, in mg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 50 ml. Note that the data will be in mg of titanium. Convert to titanium dioxide by multiplying with the molecular weight ratio, 79.89/47.9 = 1.667.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.4 Bond, A.M. "Use of Ammonium Fluoride in Determination of Zirconium and Other Elements by Atomic Absorption Spectrometry in the Nitrous Oxide-Acetylene Flame", Anal. Chem. 42, 932 (1970).

Vanadium, V_2O_5 Dust

Analyte:	**Vanadium Oxides**	**Method No.:**	S391
Matrix:	**Air**	**Range:**	0.24 - 0.90 mg/cu m
OSHA Standard:	0.5 mg/cu m - Ceiling	Precision ($\overline{CV}_T$):	0.065
Procedure:	Filter collection, Base dissolution, Flameless AAS/HGA	Validation Date:	12/24/76

1. Principle of the Method

1.1 Vanadium oxides sample collected on mixed cellulose ester membrane filter is dissolved from the sample-containing filter by heating in a sodium hydroxide solution at 50°C for 15 minutes.

1.2 The solutions of samples and standards are analyzed by flameless atomic absorption spectrophotometry in a high temperature graphite atomizer (HGA). A hollow cathode lamp for vanadium is used to provide a characteristic vanadium line at 318.4 nm. The absorbance is proportional to the vanadium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.24 - 0.90 mg/cu m at an atmospheric temperature and pressure of 23°C and 765 mm Hg, using a 25-liter sample.

2.2 The OSHA standard for vanadium dust has a 15-minute ceiling value. Sampling at a nominal flow rate of 1.7 liters per minute for 15 minutes will yield 25 liters of air sample. For a sample size of 25 liters, the working range of the method is estimated to be 0.05-1 mg/cu m.

2.3 The method may be extended to higher values by further dilution of the sample solution; the absolute sensitivity of the method has not been established.

3. Interferences

3.1 There are no known spectral line interferences for the vanadium AAS assay.

3.2 The use of an alkaline dissolution method minimizes the potential interference of ferrovanadium dust.

3.3 Iron and molybdenum do not interfere with the AAS analysis even when present in the proportion of 1 part V_2O_5 to 10 parts $Fe(NO_3)_2$ or Na_2MoO_4 (Reference 11.1).

3.4 Vanadium exhibits self-absorption at 318.4. It is necessary to operate the vanadium hollow cathode lamp at low currents to minimize self-absorption (Reference 11.2).

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.24 - 0.90 mg/cu m was 0.068. This value corresponds to a 0.033 mg/cu m standard deviation at the OSHA ceiling concentration. Statistical information and details of the validation and experimental test procedures can be found in References 11.3 and 11.1.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. The analytical method recovery was found to be 105% but this value may not represent a bias in the analytical method, but rather it may be due to uncertainties in the known concentration. Supporting data on storage stability studies show that the samples are stable upon storage at room temperature for 7 days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The method is simple.

5.2 The method does not distinguish the fume.

5.3 The life of graphite tubes is limited due to the action of the 0.1 N NaOH.

5.4 The calibration curve is non-linear above an absorbance of 0.3 units (ca. 75 ng V_2O_5) and in certain cases, depending on the graphite tube characteristics, it may be necessary to alternate samples with standards of similar response to obtain reliable results.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$

at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Barometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophctometer, having a monochromator with a reciprocal linear disperson of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have a high temperature graphite atomizer (HGA) and a deuterium arc background corrector.

6.3.1 Vanadium hollow cathode lamp

6.3.2 Deuterium arc lamp

6.3.3 Purge gases: Argon (HGA), Nitrogen (Deuterium arc)

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used

6.4 Glassware, borosilicate

6.4.1 50-ml beakers with watchglass covers

6.4.2 Pipetes, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards

6.4.3 10-ml volumetric flasks

6.5 Water bath maintained at 50°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 0.1 N Sodium Hydroxide

7.3 Aqueous standard stock solutions containing 250 µg/ml of vanadium pentoxide. This solution can be prepared by dissolving 0.250 g V_2O_5 in 0.1 N sodium hydroxide and diluting to 1.0 liter with 0.1 N NaOH.

7.4 V_2O_5 working standard solution, 2.50 µg/ml. Prepare by appropriate dilution of above solution with 0.1 N sodium hydroxide. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, rinsed with tap water, then deionized water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect V_2O_5 dust, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.7 liters per minute for 15 minutes with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.2 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.2.3 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 50-ml beaker.

8.3.2 V_2O_5 dissolution. To ensure complete dissolution of V_2O_5 from the filter, add 5 ml of 0.1 N NaOH to the beaker and heat in a water bath at 50°C for 15 minutes.

8.3.3 Cool solutions and quantitatively transfer the clear solutions into a 10-ml volumetric flask.

8.3.4 Rinse each beaker at least twice with 1-2 ml portions of 0.1 N NaOH, and quantitatively transfer each rinsing to the solution in the volumetric flask.

8.3.5 Dilute all samples to 10 ml with 0.1 N NaOH.

8.3.6 Inject 25 µl of solution into a high temperature graphite atomizer. Dry at 125°C for 40 seconds, char at 500°C for 10 seconds and atomize at 2700°C for 19 seconds. Use the deuterium arc lamp to correct for "smoke" produced by the matrix. Record the absorbance at 318.4 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve if the graphite tube in use gives reproducible results.

NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible absorbance peak, it must be rejected and replaced because results so obtained are not reliable. Also, follow instrument manufacturer's recommendations for specific operating parameters.

In case a calibration curve cannot be used because of the changing characteristics of the graphite tube, it is recommended that samples be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended would be as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, ... etc.

8.3.7 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

8.4.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.4.2 Procedure for determining recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 25-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA ceiling standard) were spiked accordingly by adding an aliquot of a solution of vanadium pentoxide containing known amounts of vanadium. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 104%.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 From the standard V_2O_5 working standard solution, prepare at least six calibration standards to cover the V_2O_5 concentration range from 2 to 30 µg per 10 ml. Prepare these calibration standards fresh daily and make all dilutions with 0.1 N NaOH.

9.2 Proceed as in Section 8.3.7.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/10 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

9.4 In cases where a calibration curve could not be used reliably, determine the appropriate response factor. To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 10 ml. An alternative procedure is to determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor determined from the response of the calibration standard.

10.2 Corrections for the blank must be made for each sample

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter
μg blank = μg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2}} \times \frac{T_2}{T_1} \right)$$

where:

f = sample flow rate
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

11.1 Vanadium, V_2O_5 Dust, S391, Backup Data Report prepared under NIOSH Contract No. 210-76-0123.

11.2 Christian, Gary and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., 1970

11.3 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Direction, DLCD, dated 1/6/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45".

11.4 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1971.

11.5 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

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