NIOSH Analytical Methods for Set A Standards Completion Program

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16. Abstracts

Industrial Hygiene sampling and analytical monitoring methods validated under the joint NIOSH/OSHA Standards Completion Program for Set A are contained herein. Monitoring methods for the following compounds are included:

Acetone
2-Butanone
Cyclohexanone
Hexone
Hydrogen sulfide
Manganese
2-Pentanone

17. Key Words and Document Analysis. 17a. Descriptors

Chemical analysis
Sampling
*Acetone
*2-Butanone
*Cyclohexanone
*Hexone
*Hydrogen sulfide
*Manganese
*2-Pentanone
*Methyl Isobutyl Ketone

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17c. COSATI Field/Group

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NIOSH Analytical Methods for Set A

A joint National Institute for Occupational Safety and Health (NIOSH)/Occupational Safety and Health Administration (OSHA) Standards Completion Program will complete standards for approximately 400 air contaminants presently listed in Tables Z-1, Z-2, and Z-3 of 29 CFR Part 1910.1000 by adding other requirements of a standard required under Section 6(b)(7) and 8(c)(3) of the Occupational Safety and Health Act of 1970 (PL 91-596). These completed standards will then contain, in addition to the permissible exposure limit given in 1910.93, appropriate provisions requiring monitoring of worker exposure, engineering control, personal protection, employee training, medical surveillance, and record keeping.

As a part of the Standards Completion Program, NIOSH is engaged in a two-year study under contract CDC-99-74-45 to validate sampling and analytical procedures for use in monitoring worker exposure to substances listed in Tables Z-1, Z-2, and Z-3. These methods have been validated and are suitable for measuring airborne concentrations of these substances and thus may be used for determining compliance with the standard or the need for control, for research, or whenever there is a need to measure airborne concentrations in the workplace. These analytical methods should not be considered the only methods which may be used to evaluate worker exposure. Other methods meeting the accuracy requirements in the standard may also be used.

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

Set A

Acetone
2-Butanone
Cyclohexanone
Hexone
Hydrogen sulfide
Manganese
2-Pentanone

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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Acetone

Analyte:	Acetone	Method No.: S1
Matrix:	Air	Range: 1200-4500 mg/cu m
OSHA Standard:	1000 ppm (2380 mg/cu m)	Precision (CV_T): 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 9/13/74

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 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 the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1200-4500 mg/cu m 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 350-5000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 10 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 acetone and other substances in the air. The first section of the charcoal tube was found to hold no more than 18 mg of acetone when a test atmosphere of 4300 mg/cu m

of acetone in air was sampled at 0.2 (0.195) liter per minute. Under these experimental conditions, after 22 minutes a 5% breakthrough was observed, i.e. the concentration of acetone in the effluent was 5% (215 mg/cu m) of that in the influent (4300 mg/cu m). (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 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, with differences in polarity, one may displace another from the charcoal.

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. Hence, retention time data on a single column, or even on a number of columns, 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 (CV_T) for the total analytical and sampling method in the range of 1200-4500 mg/cu m is 0.082. The relative standard deviation of the method is 4.1%. 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 2% lower than the "true" values.

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 trap 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 An approved and 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 (4 ft x 1/4 in) packed with 50/80 mesh Porapak, Type Q.

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

6.6 One-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: 0.5-ml delivery pipets or 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 Acetone, 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 of 2 liters is recommended. This can be accomplished by sampling for 20 minutes at a rate of 0.10 liter per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

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 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 1-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, 0.5 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.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 175°C injector temperature
5. 200°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.

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 for a given compound, 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.

For this validation study, the amount injected is equivalent to that present in a 2-liter 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 absorption 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 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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 absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 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/0.5 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/0.5 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 total mg/sample.

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

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

10.6 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
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:	2-Butanone	Method No.: S3
Matrix:	Air	Range: 380-1240 mg/cu m
OSHA Standard:	200 ppm (590 mg/cu m)	Precision (CV_T): 0.072
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 9/13/74

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 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 the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 380-1240 mg/cu m at an atmospheric temperature and pressure of 25°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 70-1500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 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.

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 2-butanone and other substances in the air. The first section of the charcoal tube was found to hold no more than 19 mg of 2-butanone when a test atmosphere of 1260 mg/cu m of 2-butanone in air was sampled at 0.17 liter

per minute. Under these experimental conditions, after 86 minutes a 5% breakthrough was observed, i.e. the concentration of 2-butanone in the effluent was 5% (63 mg/cu m) of that in the influent (1260 mg/cu m). (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 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, with differences in polarity, one may displace another from the charcoal.

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. Hence, retention time data on a single column, or even on a number of columns, 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 (CV_T) for the total analytical and sampling method in the range of 380-1240 mg/cu m is 0.072. The standard deviation at the OSHA standard level is 46 mg/cu m. 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% higher than the "true" values at the OSHA standard level.

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 trap 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 An approved and 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) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-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: 0.5-ml delivery pipets or 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-Butanone, 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 of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liter per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

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 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 1-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, 0.5 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.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 100°C injector temperature
5. 200°C manifold temperature (detector)
6. 50°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 for a given compound, 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.

For this validation study, the amount injected is equivalent to that present in a 10-liter 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 absorption 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 0.5 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

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

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 absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 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/0.5 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/0.5 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 total mg/sample.

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

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

10.6 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
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.

Cyclohexanone

Analyte:	Cyclohexanone	Method No.: S19
Matrix:	Air	Range: 98-392 mg/cu m
OSHA Standard:	50 ppm (200 mg/cu m)	Precision (CV_T): 0.062
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74 Classification:

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, graduated test tube and 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 the injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 98-392 mg/cu m at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 40 liter sample. Under the conditions of sample size (40 liters) the probable useful range of this method is 10- 500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 20 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 value in mg/sample for styrene is approximately 26 mg/sample based on breakthrough results for dry air. This value is the approximate number of milligrams of the compound which the front section will hold before the effluent level reaches 5% of the influent level. (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 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, with differences in polarity, one may displace another from the charcoal.

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. Hence, retention time data on a single column, or even on a number of columns, 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 (CV_T) for the total analytical and sampling method in the range of 98-392 mg/cu m is 0.062. The standard deviation at the OSHA standard level is 7.4 mg/cu m. 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 6.3% lower than the "true" values at the OSHA standard level.

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.

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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 trap 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 An approved and 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) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-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: 0.5-ml delivery pipets or 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 Cyclohexanone, 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 of 40 liters is recommended. This can be accomplished by sampling for 40 minutes at a rate of 1 liter per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

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 before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the analyte 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 1-ml stoppered volumetric flask. The separating section of foam is removed and discarded; the second section is transferred to another stoppered flask. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 220°C injector temperature
5. 255°C manifold temperature (detector)
6. 110°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 for a given compound, 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. The amount injected is equivalent to that present in a 40-liter sample at a concentration equal to the OSHA standard.

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 absorption 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 0.5 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

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

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 10.3 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 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/0.5 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/0.5 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 These values are further corrected for the desorption efficiency at the level of the analyte measured. Divide this total weight by the desorption efficiency as determined from the curve (See 8.5.2) to obtain the total mg/sample.

Corrected mg = mg/desorption efficiency

10.4 Add the corrected amounts present in the front and backup sections of the same sample tube to determine the total measured amount in the sample.

10.5 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V,n = V \times P/760 \times 298/(T+273)$$

where:

V,n = 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 degree centigrade

10.6 The concentration of the analyte in the air sampled (corrected to standard conditions of 25°C and 760 mm Hg) can be expressed in mg per cu m, which is numerically equal to micrograms per liter of air

mg/cu m = total mg (Section 10.4) x 1000 (liter/cu m)/V,n

10.7 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg), defined as milliliter of analyte per cubic meter of air

$$ppm = mg/cu\ m \times 24.45/MW$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound

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.

Hexone
(Methyl Isobutyl Ketone)

Analyte:	Hexone	Method No.: S18
Matrix:	Air	Range: 208-836 mg/cu m
OSHA Standard:	100 ppm (409 mg/cu m)	Precision (CV_T): 0.064
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74

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 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 the injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 208-836 mg/cu m at an atmospheric temperature and pressure 23°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 40-1230 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 12 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency decreases with decreasing loading of hexone on activated charcoal.

   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 hexone and other substances in the air. The first section of the charcoal tube was found to hold no more than 20 mg of hexone when a test atmosphere of 1145 mg/cu m

of hexone in air was sampled at 0.19 liter per minute. Under these experimental conditions, after 91.7 minutes a 5% breakthrough was observed, i.e. the concentration of hexone in the effluent was 5% (57 mg/cu m) of that in the influent (1145 mg/cu m). (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 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, with differences in polarity, one may displace another from the charcoal.

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. Hence, retention time data on a single column, or even on a number of columns, 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 (CV_T) for the total analytical and sampling method in the range of 208-836 mg/cu m is 0.064. The standard deviation at the OSHA standard level is 17 mg/cu m. 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 4.8% lower than the "true" values at the OSHA standard level.

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 trap 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 An approved and 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) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-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: 0.5-ml delivery pipets or 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 Hexone, 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 of 10 liters is recommended. This can be accomplished by sampling for 50 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.

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 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 1-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, 0.50 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.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 260°C injector temperature
5. 193°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 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 for a given compound, 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.

For this validation study, the amount injected is equivalent to that present in a 10-liter 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 absorption 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 0.5 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

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

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 absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 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/0.5 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/0.5 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 total mg/sample.

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

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

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

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

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

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

Hydrogen Sulfide

Analyte:	Hydrogen Sulfide	Method No.: S4
Matrix:	Air	Range: 8.5-63 mg/cu m
OSHA Standard:	20 ppm (30 mg/cu m) - Ceiling 50 ppm (70 mg/cu m) - Peak	Precision ($\overline{CV}_T$): 0.121
Procedure:	Absorption - Methylene Blue Spectrophotometric	Validation Date: 9/13/74

1. Principle of the Method

1.1 Hydrogen sulfide is collected by aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide (Reference 11.1). The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. STRactan 10® is added to the cadmium hydroxide slurry to minimize photo-decomposition of the precipitated cadmium sulfide (Reference 11.2). The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with an acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride (References 11.3, 11.4, 11.5).

1.2 Collection efficiency is variable below 10 µg/cu m and is affected by the type of scrubber, the size of the gas bubbles, and the contact time with the absorbing solution and the concentration of hydrogen sulfide (References 11.6, 11.7, 11.8).

2. Range and Sensitivity

2.1 This method was validated over the range of 8.5-63 mg/cu m at an atmospheric temperature and pressure of 25°C and 760 mm Hg, using a 2 liter sample. Under the conditions of sample size (2 liters) the probable useful range of the method is 5-100 mg/cu m. For sample concentrations outside this range the sampling volume should be modified.

3. Interferences

3.1 The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in ambient air. Strong

reducing agents (e.g. SO_2) inhibit color development. Even sulfide solutions containing several micrograms sulfite per ml show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10 μg/ml color formation is retarded. The use of 0.5 ml of ferric chloride solution during analysis eliminates the SO_2 interference up to 40 μg/ml.

3.2 Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 μg/ml or more. No interference is encountered when 0.3 ppm NO_2 is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide-STRactan 10®. If H_2S and NO_2 are simultaneously aspirated through cadmium hydroxide-STRactan 10® slurry, lower H_2S results are obtained, probably because of gas phase oxidation of the H_2S prior to precipitation as CdS (Reference 11.8).

3.3 Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as CdS by 15 per cent (Reference 11.8).

3.4 Substitution of other cation precipitants for the cadmium in the absorbent (i.e. zinc, mercury, etc.) will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

3.5 Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1 per cent STRactan® to the absorbing solution prior to sampling (Reference 11.2).

3.6 The choice of impinger used to trap H_2S with the $Cd(OH)_2$ slurry is very important when measuring concentration in the range 5-100 mg/cu m. Impingers or bubblers having fritted-end gas delivery tubes are a problem source if the sulfide in solution is oxidized to free sulfur by oxygen from the atmosphere. The sulfur collects on the fritted glass membrane and may significantly change the flow rate of the air sample through the system. One way of avoiding this problem is to use a midget impinger with standard glass-tapered tips.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.5-63 mg/cu m was 0.121. This value corresponds to a 3.6 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 11.9.

4.2 On the average the values obtained using the overall sampling and analytical method were 10% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 Effect of Light and Storage - Disadvantage

5.1.1 Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline, aqueous sulfide solutions are very unstable, because sulfide ion is rapidly oxidized by exposure to the air.

5.1.2 Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photo-decomposition. Losses of 50-90 per cent of added sulfide have been routinely reported by a number of laboratories. Even though the addition of STRactan 10® to the absorbing solution controls the photo-decomposition (Reference 11.2), it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or an aluminum foil wrapping.

6. Apparatus

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

6.1.1 A graduated 25-ml midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent. The impinger should be wrapped in aluminum foil to protect the sample from exposure to light.

6.1.2 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. The sampling pump is protected from splashover or water condensation by an adsorption 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 or rotameter capable of measuring 2 liters of air at 0.2 liter per minute with an accuracy of ±5%. Instead of these, calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.7 atmospheric pressure differential across the needle (Reference 11.10).

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Associated laboratory glassware.

6.3 Colorimeter with red filter or spectrophotometer at 670 nm.

6.4 Matched cells, 1-cm path length.

7. Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water.

All reagents should be refrigerated when not in use.

7.1 Amine-sulfuric Acid Stock Solution. Add 50 ml concentrated sulfuric acid to 30 ml water and cool. Dissolve 12 g of N,N-dimethyl-p-phenylene-diamine dihydrochloride* (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

7.2 Amine Test Solution. Dilute 25 ml of the Stock Solution to 1 liter with 1:1 sulfuric acid.

7.3 Ferric Chloride Solution. Dissolve 100 g of ferric chloride, $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 ml.

7.4 Ethanol, 95%.

7.5 STRactan 10®. (Arabinogalactan) Available from Stein-Hall and Company, Inc., 385 Madison Avenue, New York, New York. Arabinogalactan sold under other brand names may be used.

7.6 Cadmium Sulfate-STRactan® Solution. Dissolve 8.6 g of $3CdSO_4 \cdot 8H_2O$ in approximately 600 ml of water. Add 20 g STRactan 10® and dilute to 1 liter.

7.7 Sodium Hydroxide Solution. Dissolve 0.6 g sodium hydroxide in approximately 600 ml of water and dilute to 1 liter.

7.8 Cadmium Hydroxide-STRactan® Absorbing Solution. This absorbing solution is prepared by pipeting 5 ml of cadmium sulfate-STRactan® solution (7.6) and 5 ml of sodium hydroxide solution (7.7) directly into the midget impinger and mixing. This solution is stable for 3 to 5 days.

7.9 Stock Sodium Sulfide Standard. Place 35.28 g of $Na_2S \cdot 9H_2O$ into a 1 liter volumetric flask and add enough oxygen free distilled water to bring the volume to 1 liter. Store under nitrogen and refrigerate. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 4700 µg sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

* 10.5 g N,N-dimethyl-p-phenylenediamine oxalate may be used.

7.10 Working Sodium Sulfide Solution. Dilute 25 ml of stock solution (7.9) with oxygen free water to 250 ml. This solution contains the sulfide equivalent of approximately 500 μg/ml of H_2S. Make fresh working sulfide solution daily. The actual concentration of this solution can be determined from the titration results on the stock sodium sulfide standard (7.9).

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (Reference 11.14).

8. Procedure

8.1 Cleaning of Equipment. All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

8.2 Collection and Shipping of Samples

8.2.1 Prepare 10 ml of absorbing solution as described in Section 7.8 directly in the midget impinger. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10®). In addition, 1 or 2 Teflon demister discs may be slipped up over the impinger air inlet tube to a height approximately 1 to 2" from the top of the tube. Wrap the impinger with aluminum foil.

8.2.2 Connect the impinger (via the absorption tube) to the sampling pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used.

8.2.3 Air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.4 At the ceiling and peak concentrations, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.2.5 Turn on the pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible.

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

8.2.7 After sampling, the impinger stem must not be removed since it contains CdS deposits. It is necessary to ship the impingers with the stems in so the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e. taped) to secure the top tightly.

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

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

8.2.10 A "blank" impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this impinger.

8.3 Analysis

8.3.1 Remove the impinger top and drain it thoroughly into the impinger bottom. Set aside. Transfer the solution and deposit in the impinger bottom to a 250-ml volumetric flask. Using 50 ml of distilled water rinse the bottom twice with the aid of a clean rubber policeman on a glass stirring rod. Add the rinse solutions to the volumetric flask. With the aid of the rubber policeman wash the outside of the impinger stem with 20 ml of distilled water and add the washings to the flask and drain 20 ml of distilled water through it into the flask. The total wash water volume should be 90 ml.

8.3.2 Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the CdS deposited inside the inlet tube. Mix gently to avoid loss of H_2S.

8.3.3 Add 0.5 ml of ferric chloride solution and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

8.3.4 Prepare a zero reference solution in the same manner using a 10-ml volume of absorbing solution, through which no air has been aspirated.

8.3.5 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

9. Calibration and Standards

9.1 Aqueous Sulfide

9.1.1 Place 5 ml of each of the absorbing solutions (Sections 7.6 and 7.7) into each of a series of 250 ml volumetric flasks. Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, 160 µg of hydrogen sulfide to the different flasks.

9.1.2 Add 90 ml of distilled water.

9.1.3 Add 15 ml of amine-acid test solution to each flask and mix gently.

9.1.4 Add 0.5 ml of ferric chloride solution to each flask. Mix, make up to volume, and allow to stand for 20 minutes.

9.1.5 Determine the absorbance in a spectrophotometer at 670 nm against the sulfide-free reference solution.

9.1.6 Prepare a standard curve of absorbance versus µg H_2S.

9.2 Gaseous Sulfide. Cylinders of hydrogen sulfide in dry nitrogen in the range desired are available commercially, and may be used to prepare calibration curves for use at the 10-60 mg/cu m levels. Nitrogen containing hydrogen sulfide in the 450-600 mg/cu m range can be diluted to the desired concentrations. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

9.2.1 Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/cu m.

9.2.2 To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves and flow meters for the nitrogen and for a dry air diluent stream. All stainless steel, glass or rubber tubing must be used for the hydrogen sulfide mixture. Flow of hydrogen sulfide in nitrogen is controlled by a needle valve operated in conjunction with a previously calibrated flow meter in the range of 0.2 to 2.0 liters per minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flow meter combination in the range of 1 to 20 liters per minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric

pressure, from which they flow through a baffle tube in which mixing takes place into a 1 liter sampling flask which is provided with one or more nipples from which samples can be taken. Sampling is done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate.

9.2.3 Procedure for Preparing Simulated Calibration Curves. The following description represents a typical procedure for air sampling of short duration.

1. The system is designed to provide an accurate measure of hydrogen sulfide in the 10-60 mg/cu m range. It can be easily modified to meet special needs.

2. The dynamic range of the colorimetric procedure fixes the total volume of the sample at 2 liters; then, to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in mg/cu m, select a constant sampling time. This fixing of the sampling time is desirable also from a practical standpoint. In this case, select a sampling time of 10 minutes. To obtain a 2 liter sample of air requires a flow rate of 0.2 liter per minute. The concentration of standard H_2S in air is computed as follows:

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

where:

C = concentration of H_2S in mg/cu m

c = concentration of H_2S in nitrogen, before dilution

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

f = flow of H_2S in nitrogen, as measured by calibrated flow meter.

9.2.4 Commercially prepared hydrogen sulfide in nitrogen can be obtained with a known concentration, as analyzed by the laboratory preparing the gas. If it is desired to check this concentration, measured volume of the gas can be bubbled through the absorbing solutions, and the collected sulfide titrated against iodine-thiosulfate. The volume of gas can be measured using a wet test meter.

9.2.5 If hydrogen sulfide is present at much lower concentrations (1.5 to 140 μg/cu m), commercially available permeation tubes containing liquified hydrogen sulfide may be used to prepare calibration tubes (Reference 11.8, 11.11, 11.12, 11.13, 11.14).

10. Calculations

10.1 Gaseous Sulfide

10.1.1 Using the Beers-Law Standard curve of absorbance versus μg H_2S determine μg H_2S in the sampling impinger corresponding to its absorbance reading at 670 nm.

10.1.2 The concentration of H_2S in the air sampled can be expressed in mg/cu m which is numerically equal to μg/liter.

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\mu\text{g } H_2S \text{ (Section 10.1)}}{\text{Air volume sampled (liter)}}$$

10.1.3 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)

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MANGANESE AND COMPOUNDS (as Mn)

Analyte:	Manganese	Method No:	S5
Matrix:	Air	Range:	2.5 - 10 mg/cu m
OSHA Standard:	5 mg/cu m (ceiling)	Precision ($\overline{CV}_T$):	0.065
Procedure:	Filter collection Acid digestion Atomic absorption	Validation Date:	8/23/74

1. Principle of the Method

1.1 Samples are ashed using nitric acid to destroy the organic matrix and the manganese (including manganese compounds) is then solubilized in a hydrochloric acid solution maintaining a pH of 1.

1.2 The solutions (samples and standards) are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrometer flame. A hollow cathode lamp for manganese provides the characteristic and most intense line at 2795 nm. The absorption of this line by the ground state atoms in the flame is proportional to the manganese concentration in the aspirated sample.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.5 - 10 mg/cu m at an atmospheric temperature and pressure of 24°C and 749 mm Hg, using a 20 - 26 liter sample. Under the conditions of sample size (22.5 liters), the working range of the method is estimated to be 0.2 - 20 mg/cu m.

2.2 The sensitivity of this method using the 100 ml final assay solution volume should be adequate for most cases. Since the standard is a ceiling value, measurement of lower atmospheric concentrations should be made by using smaller final solution volumes. The method may similarly be extended to higher values by further dilution of the sample.

3. Interferences

There are no known interferences for the manganese 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 2.5 - 10 mg/cu m was 0.065. This value corresponds to a 0.30 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 On the average the values obtained using the overall sampling and analytical method were 9% lower than the "true" value at the OSHA standard level.

5. Advantages and Disadvantages

(not applicable)

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% (reference 11.4) 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 monochromotor with a reciprocal linear dispersion of about 6.5 Å/mm in the ultraviolet region. The instrument must have the necessary burner heads for the indicated flame.

6.3.1 Manganese hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: purified 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

6.4.4 125 ml polyethylene bottles

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, 1:1 aqueous solution

7.4 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of Manganese.

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 by immersion in chromic acid (a saturated solution of sodium dichromate in concentrated sulfuric acid) and then rinsed thoroughly with warm tap water, concentrated nitric acid, 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 Sampling Requirements and Shipping of Samples

8.2.1 The OSHA standard (ceiling value) for manganese is 5 mg/cu m.

8.2.2 To collect particulate manganese 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.

8.2.3 Sample size: A series of 15 minute samples at a sampling rate of 1.5 lpm is required since the standard is limited to a ceiling value.

8.2.4 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.

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

8.3 Analysis of Samples

8.3.1 Transfer each sample to a clean 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 most of the acid has evaporated. Repeat this process two more times using 2 ml of concentrated nitric acid each time. It is advisable not to allow the solution to evaporate to dryness.

8.3.3 Manganese dissolution: To ensure complete dissolution of manganese compounds, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). Do this digestion process

by three successive additions of 2 ml of aqueous HCl, followed by evaporation to about 0.5 ml after each addition. It is suggested that the solution should not be allowed 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 100 ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 10 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 100 ml with distilled water.

8.3.7 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 2795 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 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 in accordance with the total procedure.

9. Calibration and Standards

9.1 From each of the 1000 µg/ml stock manganese standard solutions, prepare at least 4 working standards to cover the range from 0.05 to 4 µg/ml. All standard solutions are made 0.3 N in HCl and are stored in polyethylene bottles. Since the low concentration standards may deteriorate, the standard solutions should be remade each day.

9.2 Aspirate each of the standards 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/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.

DOCUMENT PRODUCTION DIVISION
REPRODUCTION CONTROL
DAILY PRODUCTION REPORT

DATE: 3-19-98

OPERATOR: S-STAFFORD **CODE**

HOURS ASSIGNED:	SHIFT: N (D) O	LEAVE: A S O		OTHER HOURS	TOTAL PRODUCTION HRS.

PRINT REQUESTS	DOC	HRS.	PAG.	ADSTAR SCANNED ACCESSION NUMBERS\PAGES --- SCANNER:											
113's - REGULAR				PB91916501	74	ADA248644	48								
113's - RUSH				PB96963303	102	ADA160733	34								
BACKORDER				ADA137873	64	ADA202343	10								
ADSTAR SCAN ONLY				N9435947	18	ADA191435	60								
BX - RUSH\SPECIAL				[illegible]	[illegible]	[illegible]									

10. Calculations

10.1 From the calibration curve, r the analyzed samples.

10.2 Blank values, if any, are to sample value.

10.3 Convert the volume of air col 25°C and 760 mm Hg as follows

$$V_n = V \times \frac{P}{760} \times$$

where:

V_n = volume of
V = volume of
P = Barometric
T = Temperatur

10.4 To determine the concentratio served solution concentration tion volume which was used fo ume of air sampled (in liters of 25°C and 760 mm Hg).

$$\text{Mn mg/cu m} = \frac{\mu g\ M}{1}$$

11. References

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11.2 Methods for Emission Spectroc E-2, Philadelphia, 1971.

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11.4 NIOSH TR (pump reference)

2-Pentanone

Analyte:	2-Pentanone	Method No.:	S20
Matrix:	Air	Range:	395-1570 mg/cu m
OSHA Standard:	200 ppm (705 mg/cu m)	Precision (CV_T):	0.063
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/8/74

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 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 the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 395-1570 mg/cu m at an atmospheric temperature and pressure of 24°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 70-2100 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 21 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency decreases with decreasing loading of 2-pentanone on activated charcoal.

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 2-pentanone and other substances in the air. The first section of the charcoal tube was found to hold no more than 27 mg of 2-pentanone when a test atmosphere

50<

of 1450 mg/cu m of 2-pentanone in the air was sampled at 0.19 liter per minute. Under these experimental conditions, after 100 minutes a breakthrough was observed, i.e., the concentration of 2-pentanone in the effluent was 5% (72.5 mg/cu m) of that in the influent (1450 mg/cu m). (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 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, with differences in polarity, one may displace another from the charcoal.

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. Hence, retention time data on a single column, or even on a number of columns, 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 (CV_T) for the total analytical and sampling method in the range of 395-1570 mg/cu m is 0.063. The standard deviation at the OSHA standard level is 21 mg/cu m. 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 1.3% lower than the "true" values at the OSHA standard level.

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 trap 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 An approved and 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) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-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: 0.5-ml delivery pipets or 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-Pentanone, 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 of 10 liters is recommended. This can be accomplished by sampling for 50 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.

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 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 1-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, 0.50 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.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 190°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 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 for a given compound, 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.

For this validation study, the amount injected is equivalent to that present in a 10-liter 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 absorption 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 0.5 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

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

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 absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 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/0.5 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/0.5 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 total mg/sample.

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

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

10.6 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
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.

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