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HC 1435 NIOSH/OSHA Standards Completion Program

Hexane

Analyte:	Hexane	Method No.:	S90
Matrix:	Air	Range:	877 - 3679 mg/cu m
OSHA Standard:	500 ppm (1800 mg/cu m)	Precision ($\overline{CV}_T$):	0.062
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 877 - 3679 mg/cu m at an atmospheric temperature and pressure of 17°C and 764 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters), the probable useful range of this method is 180 - 5400 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 22-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 21.7 mg of analyte when a test atmosphere containing 3679 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 31 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 877 - 3679 mg/cu m was 0.062. This value corresponds to a 112 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 3.8% lower than the "true" value at the OSHA standard level.

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

5. Advantages and Disadvantages of the Method

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

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

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

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

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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

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

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

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 n-Hexane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

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

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

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

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

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

A similar procedure is followed for the backup sections.

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

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

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

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

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

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

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

where:

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

11. References

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

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

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

Sampling Data Sheet No. S90

Substance

Hexane

Standard

8-hour time-weighted average: 500 ppm (1800 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the hexane vapors present. The analyte is desorbed from the charcoal with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 877 - 3679 mg/cu m for a 4-liter sample at 17°C and 764 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, ±5%, over the range 0.05 to 0.2 liters per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 4 liters is recommended. Sample at a flow rate of 0.2 liters per minute or less.

Sampling Procedure

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

2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

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

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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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 tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

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6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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

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

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

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 n-Hexane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

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

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

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

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

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

A similar procedure is followed for the backup sections.

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

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

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

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

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

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

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

where:

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

11. References

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

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

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

Sampling Data Sheet No. S90

Substance

Hexane

Standard

8-hour time-weighted average: 500 ppm (1800 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the hexane vapors present. The analyte is desorbed from the charcoal with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 877 - 3679 mg/cu m for a 4-liter sample at 17°C and 764 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, ±5%, over the range 0.05 to 0.2 liters per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 4 liters is recommended. Sample at a flow rate of 0.2 liters per minute or less.

Sampling Procedure

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

2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

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

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. One charcoal tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank.

Special Consideration

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

2. Due to the high resistance of the charcoal tube, this sampling method placed a heavy load on the sampling pump. Therefore, no more than ten charcoal tube samples should be taken without fully recharging the battery.

3. If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

4. The desorption efficiency of charcoal varies from batch to batch. Therefore, all the tubes used to collect a set of samples should contain charcoal from the same batch. Several unused charcoal tubes should accompany the samples. Information on the batch number of the charcoal must be supplied.

Bulk Samples

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

Shipping Instructions

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

Reference

Hexane, NIOSH Method No. S90

Backup Data Report

Substance: Hexane

OSHA Standard: 1800 mg/cu m

Chemical used for
validation: n-Hexane, Fisher 99 Mol % Pure

Procedure

The general procedure used is described in NIOSH Method No. S90 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of hexane represented in a 4-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 376 mg/min of hexane via a syringe injector to a dry air stream flowing at a rate of 0.1022 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to held 21.7 mg of hexane when a test atmosphere containing 3679 mg/cu m of hexane in air was sampled at 0.19 liters per minute for 31 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0139 \qquad \overline{CV}_2 = 0.0368 \qquad \overline{CV}_T = 0.0623$$

The average recovery of the generated samples over all levels was

97.9 ± 8.1%

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (0.07)^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

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

Date Sheet: Hexane S90

Analysis

Level 0.5S			1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
3.56	3.48	0.978	7.25	6.88	0.949	14.50	13.86	0.956
3.56	3.33	0.935	7.25	6.84	0.943	14.50	13.81	0.952
3.56	3.35	0.941	7.25	6.85	0.945	14.50	13.65	0.941
3.56	3.36	0.944	7.25	6.98	0.963	14.50	13.98	0.964
3.56	3.32	0.933	7.25	6.75	0.931	14.50	13.68	0.943
3.56	3.34	0.938	7.25	6.73	0.928	14.50	13.75	0.948

	0.5S	1S	2S
n =	6	6	6
mean	0.945	0.943	0.951
std dev	0.0167	0.0127	0.0086
CV_1	0.0177	0.0135	0.0090

$\overline{CV}_1$ 0.0139

$\overline{CV}_{A+\overline{DE}}$ 0.0150

Data Sheet: Hexane S90
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.29	3.48	3.97	877	877	
	3.25	3.44	3.97	867	877	
	1.53*	1.62*	3.97	409*	877	
	3.10	3.28	3.97	826	877	
	2.93	3.10	3.97	780	877	
	3.25	3.44	3.97	867	877	
			n = 5			
			mean	843		96.1
			std dev	40.5		
			CV_2	0.0481		
1S	6.37	6.73	3.97	1695	1808	
	6.42	6.79	3.94	1723	1808	
	6.56	6.93	3.90	1777	1808	
	6.89	7.28	4.01	1815	1808	
	6.09	6.44	3.96	1626	1808	
	6.64	7.02	3.89	1805	1808	
			n = 6			
			mean	1740		96.2
			std dev	72.8		
			CV_2	0.0418		
2S	13.97	14.77	4.06	3640	3680	
	14.14	14.95	3.96	3780	3680	
	14.14	14.95	3.96	3780	3680	
	13.98	14.78	3.94	3750	3680	
	14.61	15.44	4.10	3770	3680	
	14.05	14.85	3.96	3750	3680	
			n = 6			
			mean	3745		101.6
			std dev	53.2		
			CV_2	0.0142		
			$\overline{CV}_2$	0.0368		

Analyte:	Pentane	Method No.:	S379
Matrix:	Air	Range:	1476-6190 mg/cu m
OSHA Standard:	1000 ppm (2950 mg/cu)	Precision ($\overline{CV}_T$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tub o trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph

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TITLE (PENTANE)
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Stanford Research Institute -
Center for Occupational and Envir
Safety and Health
1611 North Kent Street

Pentane

Analyte:	Pentane	Method No.:	S379
Matrix:	Air	Range:	1476-6190 mg/cu m
OSHA Standard:	1000 ppm (2950 mg/cu)	Precision ($\overline{CV}_T$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 1476-6190 mg/cu m at an atmospheric temperature and pressure of 24°C and 769 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 300-8850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 18-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 18 mg of analyte when a test atmosphere containing 5640 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 16.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1476-6190 mg/cu m was 0.055. This value corresponds to a 160 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 9.7% lower than the "true" value at the OSHA standard level.

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

5. Advantages and Disadvantages of the Method

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

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

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

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

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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

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

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

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Pentane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

8.3.5 A maximum sample size of 2 liters is recommended. Sample at a rate of 0.05 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

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

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

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

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 2-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

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

A similar procedure is followed for the backup sections.

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

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

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

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

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

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

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

where:

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

11. References

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

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

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

Sampling Data Sheet No. S379

Substance

Pentane

Standard

8-hour time-weighted average: 1000 ppm (2950 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the pentane vapors present. The analyte is desorbed from the charcoal with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 1476-6190 mg/cu m for a 2-liter sample at 24°C and 769 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, ±5%, over the range 0.05 to 0.2 liters per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 2 liters is recommended. Sample at a flow rate of 0.05 liters per minute or less.

Sampling Procedure

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

2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

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

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. One charcoal tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank.

Special Consideration

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

2. Due to the high resistance of the charcoal tube, this sampling method placed a heavy load on the sampling pump. Therefore, no more than ten charcoal tube samples should be taken without fully recharging the battery.

3. If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

4. The desorption efficiency of charcoal varies from batch to batch. Therefore, all the tubes used to collect a set of samples should contain charcoal from the same batch. Several unused charcoal tubes should accompany the samples. Information on the batch number of the charcoal must be supplied.

Bulk Samples

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

Shipping Instructions

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

Reference

Pentane, NIOSH Method No. S379

Backup Data Report

Substance: Pentane

OSHA Standard: 2950 mg/cu m

Chemical used for
validation: Pentane, MC/B Chromatoquality

Procedure

The general procedure used is described in NIOSH Method No. S379 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of pentane represented in a 2-liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report. For pentane, the back-up section of the charcoal tubes was also desorbed with 1.0 ml of carbon disulfide and analyzed in the usual manner. No evidence of pentane was found in the back-up sections of all the samples collected.

Modification

There were no major modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 603.1 mg/min of pentane via a syringe injector to a dry air stream flowing at a rate of 0.0975 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.067 liters per minute for 30 minutes (2 liters). The data reported are from the second set of 18 samples collected. The data for the first set of 18 samples gave a CV_2 of 0.040, but a low average recovery - 86.8%. Note that for the second set of samples, the generator concentration was determined not only on the basis of the syringe delivery rate and air flow as noted above, but also by measuring the main line (2S) hydrocarbon concentration with a Beckman Model 402 Hydrocarbon Analyzer properly calibrated using reference gas standards. The pentane concentration by the former method is 6190 mg/cu m and agrees well with the total hydrocarbon data - 6170 mg/cu m.

Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 18 mg of pentane when a test atmosphere containing 5640 mg/cu m of pentane in air was sampled at 0.19 liters per minute for 16.5 minutes; Breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X and 2X the OSHA standard for sampling and analysis was applied to the data for pentane as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 15.65 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for pentane show excellent precision. Therefore pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0141 \qquad \overline{CV}_2 = 0.0229 \qquad \overline{CV}_T = 0.0549$$

The average recovery of the generated samples over all levels was

$$91.7 \pm 8.0\%$$

The uncertainty in this value was computed as follows:

$$\%\ \text{Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (0.07)^2} \times 100}{\%\ \text{Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Pentane S379

Analysis

Level 0.5S			1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
2.983	2.898	0.972	5.97	5.60	0.938	11.81	11.70	0.991
2.983	2.897	0.971	5.97	5.76	0.965	11.81	11.45	0.970
2.983	2.893	0.970	5.97	5.74	0.961	11.81	11.13	0.942
2.983	2.928	0.982	5.97	5.67	0.950	11.81	11.37	0.963
2.983	2.930	0.982	5.97	5.62	0.941	11.81	11.35	0.961
2.983	2.923	0.980	5.97	5.85	0.980	11.81	11.30	0.957

n =	6	6	6
mean	0.976	0.956	0.964
std dev	0.00574	0.0159	0.0162
CV_1	0.00588	0.0167	0.0163

$\overline{CV}_1$ 0.0141

$\overline{CV}_{A+\overline{DE}}$ 0.0152

Data Sheet: Pentane S379
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	2.633	2.728	2.00	1364	1476	
	2.655	2.751	1.97	1396	1476	
	2.852	2.955	2.08	1421	1476	
	2.775	2.876	2.14	1344	1476	
	2.877	2.981	2.15	1387	1476	
	2.637	2.733	2.11	1295	1476	
			n = 6			
			mean	1369		92.8
			std dev	44.4		
			CV_2	0.0325		
1S	5.39	5.59	2.03	2754	3040	
	5.39	5.59	2.00	2795	3040	
	5.09	5.28	2.00	2640	3040	
	5.13	5.32	1.94	2742	3040	
	5.28	5.47	1.97	2777	3040	
	5.24	5.43	1.97	2756	3040	
			n = 6			
			mean	2744		90.3
			std dev	54.3		
			CV_2	0.0198		
2S	10.67	11.06	1.94	5700	6190	
	10.78	11.17	1.97	5670	6190	
	10.97	11.37	2.00	5690	6190	
	11.65	12.07	2.11	5720	6190	
	10.66	11.05	1.94	5700	6190	
	10.85	11.24	1.97	5710	6190	
			n = 6			
			mean	5700		92.1
			std dev	17.22		
			CV_2	0.00302		
			$\overline{CV}_2$	0.0220		

Analyte:	Heptane	Method No.:	S89
Matrix:	Air	Range:	968-4060 mg/cu m
OSHA Standard:	500 ppm (2000 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

---

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with

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DATE OF REQUEST [illegible] 24 '78

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SRI NO.	YEAR	INITIAL PAGE NO.	SR. AUTHOR	ABBREVIATED JOURNAL TITLE
HCx1472	1975	S89-1	Anon	NIOSH ANALYTICAL METHODS

TITLE (HEPTANE) ~~(DOCUMENTATION OF NIOSH VALIDATION TESTS)~~ NIOSH CONTRACT No. CDC 99-74-45. U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE, PUBLIC HEALTH SERVICE, CENTER FOR DISEASE CONTROL, NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH, PHYSICAL AND CHEMICAL ANALYSIS BRANCH, 1975, S89-1.

AUTHORS

FULL REFERENCE

VOL. ISS. NO. PAGES S89-1 to S89-9 NIOSH ANALYTICAL METHODS

DATE OF PUB. 1 /1975

NIOSH NO.

HCx 1472

FOREIGN LANG. CROSS REF. NO.

WARNING CODE

Stanford Research Institute -
Center for Occupational and Envir
Safety and Health
1611 North Kent Street
Arlington, Virginia 22209

Analyte:	Heptane	Method No.:	S89
Matrix:	Air	Range:	968-4060 mg/cu m
OSHA Standard:	500 ppm (2000 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

---

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 968-4060 mg/cu m at an atmospheric temperature and pressure of 24°C and 748 mm Hg, using a 4 liter sample. Under the conditions of sample size (4 liters) the probable useful range of this method is 200-6000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 24 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 24.7 mg of analyte when a test atmosphere containing 4060 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 32 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 968-4060 mg/cu m was 0.056. This value corresponds to a 112 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 6.5% lower than the "true" value at the OSHA standard level.

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

5. Advantages and Disadvantages of the Method

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

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

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

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

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 on 100/120 mesh Supelcoport.

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

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

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

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Heptane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

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

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

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

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

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

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

Calibration and Standards

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

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

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

A similar procedure is followed for the backup sections.

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

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

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

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

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

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

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

where:

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

11. References

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

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

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

Sampling Data Sheet No.S89

Substance

Heptane

Standard

8-hour time-weighted average: 500 ppm (2000 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the heptane vapors present. The analyte is desorbed from the charcoal with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 968-4060 mg/cu m for a 4 liter sample at 24°C and 748 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, ±5%, over the range 0.05 to 0.2 liters per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 4 liters is recommended. Sample at a flow rate of 0.2 liters per minute or less.

Sampling Procedure

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

2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

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

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. One charcoal tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank.

Special Consideration

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

2. Due to the high resistance of the charcoal tube, this sampling method placed a heavy load on the sampling pump. Therefore, no more than ten charcoal tube samples should be taken without fully recharging the battery.

3. If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

4. The desorption efficiency of charcoal varies from batch to batch. Therefore, all the tubes used to collect a set of samples should contain charcoal from the same batch. Several unused charcoal tubes should accompany the samples. Information on the batch number of the charcoal must be supplied.

Bulk Samples

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

Shipping Instructions

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

Reference

Heptane, NIOSH Method No.S89

Backup Data Report

Substance: Heptane

OSHA Standard: 2000 mg/cu m

Chemical used for
  validation: Heptane, Fisher Certified

Procedure

The general procedure used is described in NIOSH Method No. S89 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of heptane represented in a 4 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 408 mg/min of heptane via a syringe injector to a dry air stream flowing at a rate of 0.1005 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2364, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 24.7 mg of heptane when a test atmosphere containing 4060 mg/cu m of heptane in air was sampled at 0.19 liters per minute for 32 minutes; breakthrough was observed at this time, i.e., concentration of analyte in the effluent was 5% of that in the influent.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for heptane as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 9.92 indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for heptane show excellent precision. Therefore pooling will not introduce significant error. For this reason CV_T is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0161 \qquad \overline{CV}_2 = 0.0233 \qquad \overline{CV}_T = 0.0556$$

The average recovery of the generated samples over all levels was

$93.5 \pm 7.9\%$

The uncertainty in this value was computed as follows:

$$\% \text{ Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (0.07)^2} \times 100}{\% \text{ Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

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

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Heptane S89

Analysis

Level	0.5S			1S			2S	
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.08	4.03	0.988	8.15	8.12	0.996	16.31	15.66	0.960
4.08	3.93	0.963	8.15	7.86	0.964	16.31	15.60	0.956
4.08	3.90	0.956	8.15	7.76	0.952	16.31	15.47	0.948
4.08	3.83	0.939	8.15	7.76	0.952	16.31	15.54	0.953
4.08	*	*	8.15	7.65	0.939	16.31	15.55	0.953
4.08	3.87	0.949	8.15	7.80	0.957	16.31	15.51	0.951

n =	5	6	6
mean	0.959	0.960	0.954
std dev	0.0185	0.0194	0.00414
CV_1	0.0193	0.0203	0.00433

$\overline{CV}_1$ 0.0161

$\overline{CV}_{A+\overline{DE}}$ 0.0174

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*Lost Sample

Data Sheet: Heptane S89
Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	3.53	3.68	4.09	900	968	
	3.36	3.51	4.09	858	968	
	3.53	3.68	4.09	900	968	
	3.54	3.70	4.09	905	968	
	3.26	3.40	4.09	831	968	
	3.56	3.72	4.09	910	968	
			n = 6			
			mean	884		91.3
			std dev	32.0		
			CV_2	0.0362		
1S	7.40	7.72	4.09	1888	1996	
	7.20	7.52	4.05	1857	1996	
	7.21	7.53	4.02	1873	1996	
	7.45	7.78	4.16	1870	1996	
	7.32	7.64	4.11	1859	1996	
	7.21	7.53	4.07	1850	1996	
			n = 6			
			mean	1866		93.5
			std dev	13.67		
			CV_2	0.00733		
2S	15.53	16.21	4.22	3840	4060	
	15.63	16.32	4.11	3970	4060	
	15.38	16.05	4.11	3905	4060	
	15.29	15.96	4.09	3902	4060	
	15.41	16.09	4.25	3786	4060	
	15.32	15.99	4.11	3891	4060	
			n = 6			
			mean	3882		95.6
			std dev	62.8		
			CV_2	0.0162		
			$\overline{CV}_2$	0.0233		

Octane

Analyte: Octane

Matrix: Air

OSHA Standard: 500 ppm (2350 mg/cu m

Procedure: Adsorption on charcoal, desorption with carbon disulfide, GC

Method No.: S378

Range: 1050 - 4403 mg/cu m

Precision ($\overline{CV}_T$): 0.060

Validation Date: 3/14/75

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1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with

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HCX-1473	1975	S378-1	Anon	NIOSH ANALYTICAL METHODS

TLE (OCTANE) STANDARDS COMPLETION PROGRAM (~~DOCUMENTATION OF NIOSH VALIDATION TESTS~~) NIOSH

UTHORS CONTRACT NO. CDC 99-74-45. U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE, PUBLIC HEALTH

ULL REFERENCE SERVICE, CENTER FOR DISEASE CONTROL, NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH, PHYSICAL AND CHEMICAL ANALYSIS BRANCH, 1975, S378-1.

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HCX-1473

Stanford Research Institute
Center for Occupational and Enviro
Safety and Health

Analyte:	Octane	Method No.:	S378
Matrix:	Air	Range:	1050 - 4403 mg/cu m
OSHA Standard:	500 ppm (2350 mg/cu m	Precision ($\overline{CV}_T$):	0.060
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 1050 - 4403 mg/cu m at an atmospheric temperature and pressure of 20°C and 758 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters), the probable useful range of this method is 235 - 7050 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 28 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 30 mg of analyte when a test atmosphere containing 4612 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 34 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1050 - 4403 mg/cu m was 0.060. This value corresponds to a 141 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 5.2% lower than the "true" value at the OSHA standard level.

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

5. Advantages and Disadvantages of the Method

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

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

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

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

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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

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

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

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

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

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Octane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

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

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

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

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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

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

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

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

A similar procedure is followed for the backup sections.

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

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

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

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

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

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

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

where:

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

11. References

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

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

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

Sampling Data Sheet No. S378

Substance

Octane

Standard

8-hour time-weighted average: 500 ppm (2350 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the octane vapors present. The analyte is desorbed from the charcoal with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 1050 - 4403 mg/cu m for a 4-liter sample at 20°C and 758 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, ±5%, over the range 0.05 to 0.2 liters per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 4 liters is recommended. Sample at a flow rate of 0.2 liters per minute or less.

Sampling Procedure

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

2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

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

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. One charcoal tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank.

Special Consideration

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

2. Due to the high resistance of the charcoal tube, this sampling method placed a heavy load on the sampling pump. Therefore, no more than ten charcoal tube samples should be taken without fully recharging the battery.

3. If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

4. The desorption efficiency of charcoal varies from batch to batch. Therefore, all the tubes used to collect a set of samples should contain charcoal from the same batch. Several unused charcoal tubes should accompany the samples. Information on the batch number of the charcoal must be supplied.

Bulk Samples

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

Shipping Instructions

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

Reference

Octane, NIOSH Method No. S378

Backup Data Report

Substance: Octane

OSHA Standard: 2350 mg/cu m

Chemical used for
validation: Octane, Aldrich 99 + % Gold Label

Procedure

The general procedure used is described in NIOSH Method No. S378 which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1 and 2 times the OSHA standard by spiking with the appropriate volume of octane represented in a 4 liter air sample. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, Pa. Spiking and desorption tests were done in the 2 ml vials used with the Varian Model 8000 automatic sample injector. Gas chromatographic analyses were done with this autosampler using nonane as internal standard. Details of the analysis procedures may be found in the Butyl Acetate S47 Backup Data Report.

Modification

There were no modifications of P&CAM 127.

Generation

Test atmosphere samples at a concentration 2 times the OSHA standard level were generated by delivering 454 mg/min of octane via a syringe injector to a dry air stream flowing at a rate of 0.1031 cu m/min. The three sample lines were then maintained at dilution ratios of 0.2384, 0.4916 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All 6 samples at the 3 test levels were collected simultaneously at 0.22 liters per minute for 18 minutes (4 liters). Details of the sample generation and collection equipment may be found in the Butyl Acetate S47 Backup Data Report.

Breakthrough

The first section of the charcoal tube was found to hold 30 mg of octane when a test atmosphere containing 4612 mg/cu m of octane in air was sampled at 0.19 liters per minute for 34 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data are based on a prior experiment.

Precision and Accuracy

Bartlett's test for homogeneity of variances at 0.5X, 1X, and 2X the OSHA standard for sampling and analysis was applied to the data for octane as in Reference No. 2.

The sampling and analysis data gave a chi squared value of 10.9, indicating that the hypothesis of equal variance may be rejected at p (probability) less than 0.01. The data for octane show excellent precision. Therefore, pooling will not introduce significant error. For this reason $\overline{CV}_T$ is calculated on the pooled data.

The statistical procedures used are described in Reference 1.

$$\overline{CV}_1 = 0.0039 \qquad \overline{CV}_2 = 0.0321 \qquad \overline{CV}_T = 0.0595$$

The average recovery of the generated samples over all levels was

$$98.2 \pm 7.8\%$$

The uncertainty in this value was computed as follows:

$$\%\ \text{Uncertainty} = \frac{\sqrt{(\overline{CV}_2)^2 + (\overline{0.07})^2} \times 100}{\%\ \text{Recovery}/100}$$

where 0.07 is the uncertainty in the generated concentration level. This value was determined from the acetate esters in Set D.

References

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

2. Backup Data Report, Propylene Oxide, No. S75, prepared under NIOSH Contract CDC-99-74-45.

Data Sheet: Octane S378

Analysis

Level 0.5S			1S			2S		
mg added	mg found	DE	mg added	mg found	DE	mg added	mg found	DE
4.75	4.47	0.941	9.78	9.32	0.953	18.86	18.18	0.964
4.75	4.39	0.924	9.78	9.07	0.927	18.86	18.11	0.960
4.75	4.40	0.926	9.78	9.23	0.944	18.86	18.21	0.966
4.75	4.41	0.928	9.78	9.18	0.939	18.86	18.45	0.978
4.75	4.42	0.931	9.78	9.25	0.946	18.86	18.23	0.967
4.75	4.38	0.922	9.78	9.22	0.943	18.86	17.90	0.949

n =	6	6	6
mean	0.929	0.942	0.964
std dev	0.00680	0.00867	0.00949
CV_1	0.00732	0.00921	0.00984

$\overline{CV}_1$	0.00885
$\overline{CV}_{A+\overline{DE}}$	0.00956

Data Sheet: Octane S378
Sampling and Analysis

Test Level	------------- Found -------------				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	4.09	4.40	4.01	1097	1049	
	4.02	4.33	4.01	1080	1049	
	3.82	4.12	4.01	1027	1049	
	3.96	4.27	4.01	1065	1049	
	3.77	4.07	4.01	1015	1049	
	3.18*	3.44*	4.01	858*	1049	
			n = 5			
			mean	1057		100.8
			std dev	34.8		
			CV_2	0.0329		
1S	7.78	8.28	4.01	2065	2170	
	7.73	8.22	3.97	2070	2170	
	7.69	8.18	3.94	2075	2170	
	7.89	3.39	4.08	2055	2170	
	7.77	8.27	4.03	2050	2170	
	7.63	8.12	3.99	2035	2170	
			n = 6			
			mean	2058		94.8
			std dev	14.7		
			CV_2	0.00715		
2S	16.40	17.14	4.13	4150	4400	
	16.66	17.39	4.03	4320	4400	
	16.32	17.05	4.03	4230	4400	
	17.16	17.88	4.01	4460	4400	
	18.82	19.56	4.17	4690	4400	
	16.57	17.30	4.03	4290	4400	
			n = 6			
			mean	4360		98.9
			std dev	193.0		
			CV_2	0.0443		
			$\overline{CV}_2$	0.0321		

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*These values excluded from statistical analysis