IX. APPENDIX I

METHOD FOR SAMPLING ALKANES (C5-C8) IN AIR

General Requirements

To evaluate conformance with the recommended environmental limits, airborne concentrations of pentane, hexane, heptane, and octane must be measured within the individual worker's breathing zone. Sampling procedures must conform with the following criteria:

(a) Samples collected must be representative of the individual worker's exposure.

(b) Sampling data sheets must include:

(1) The date and time of sample collection.

(2) Sampling duration.

(3) Volumetric flow rate of sampling.

(4) A description of the sampling location.

(5) Ambient temperature and pressure.

(6) Other pertinent information (eg, worker's name, shift, work process).

Recommended Method

(a) Personal samples must be collected in the breathing zone of the employee without interfering with his freedom of movement and must characterize the exposure from each job or specific operation in each production area.

(b) A portable, battery-operated personal sampling pump whose flow can be accurately controlled to within 5% at 50 ml/minute and 250 ml/minute should be used in conjunction with activated charcoal tubes to collect the samples.

(c) The tube of activated charcoal should be attached to the employee. The shirt collar is convenient for this purpose.

(d) The sampling rate for TWA concentration determinations should be maintained at a value of 50 ml/minute; each sample taken to determine a TWA concentration should be collected for 80 minutes. Samples, taken to determine if airborne alkane concentrations greater than the ceiling concentration exist, should be collected at a rate of 250 ml/minute for 15 minutes.

(e) At least one unused tube of activated charcoal from the same batch as that of the tube or tubes used for sampling shall be sent to the analytical laboratory to determine the blank correction value.

Equipment for Air Sampling

(a) Battery-operated personal sampling pump: The pump should have a clip for attachment to the employee. All pumps and flowmeters must be calibrated using a calibrated test meter or other reference, as described in the section of this appendix entitled Calibration of Equipment.

(b) Charcoal tubes: Glass tubes with both ends flame-sealed, 7 cm long with a 6-mm outer diameter and a 4-mm internal diameter, containing two sections of 20/40 mesh activated coconut-shell charcoal separated by a 2-mm portion of polyurethane foam. The adsorbing section should contain 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of the polyurethane foam should be placed between the outlet end of the tube and the backup section. A plug of silyated glass wool should be placed in front of the adsorbing section.

Calibration of Equipment

Accurate calibration of the sampling pump is essential to the correct interpretation of the volume indicated. The necessary frequency of calibration is dependent upon the use, care, and handling to which the pump is subjected. Pumps should be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard use, it should be calibrated more frequently. Regardless of use, maintenance and calibration should be performed on a regular schedule and records of these should be kept.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibration instruments such as a wet test meter or dry gas meter can be used. The actual setups will be similar for all instruments.

The proper calibration setup for personal sampling pumps with charcoal-tubes is as shown in Figure XII-1. If some other calibration device is selected, an equivalent procedure should be used. Since the flow rate produced by a pump is dependent on the pressure drop across the sampling device, in this case a charcoal tube, the pump must be calibrated while operating with a representative charcoal tube in line. Instructions for calibration with the soapbubble meter are as follows:

(a) The voltage of the pump battery is checked with a voltmeter to ensure adequate voltage for calibration. The battery is charged if necessary.

(b) Both tips of a charcoal tube are broken off to produce openings of at least 2 mm in diameter.

(c) The sampling train is assembled as shown in Figure XII-1.

(d) The pump is turned on, and the inside of the soapbubble meter is moistened by immersing the buret into the soap solution and drawing bubbles up the inside until they are able to travel the entire length of the buret without bursting.

(e) The pump flow controller is adjusted to provide the desired flow rate.

(f) The water manometer is checked to ensure that the pressure drop across the sampling train does not exceed 15.2 mm of water at 50 ml/minute or 76.2 mm of water at 250 ml/minute.

(g) A soapbubble is started up the buret, and the time it takes the bubble to move from one calibration mark to another is measured with a stopwatch.

(h) The procedure described in (g) is repeated at least twice, the results averaged, and the flow rate calculated by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of air sampled is the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient of the volume between the two preselected marks divided by the number of strokes.

(i) The volume measured, the elapsed time or number of strokes, the pressure drop, the air temperature, the atmospheric pressure, the serial number of the pump, and the name of the person performing the calibration should be recorded.

Collection of Samples

(a) Both ends of a charcoal tube are broken to provide openings of at least 2 mm, which is 1/2 of the internal diameter of the tube. A smaller opening causes a limiting orifice effect which reduces the flow through the tube. The main adsorbing section of the charcoal tube should contain 100 mg of charcoal.

(b) The smaller section of charcoal (50 mg) in the tube is used as a backup adsorbing section and should therefore be placed nearest the sampling pump. Noncollapsible tubing may be used to connect the back of the tube to the pump, but no tubing should ever be put in front of the charcoal tube. During sampling, the tube should be supported in a vertical position to prevent channeling. After the sample is collected, the tube must be capped; caps are provided with commercially available tubes. Masking tape can be substituted for caps when sealing the tube. Rubber caps must never be used.

(c) The recommended sampling flow rate is 50 ml/minute for TWA concentration determinations and 250 ml/minute for ceiling concentration determinations. A 4-liter sample is normally adequate. The flow rate should be set as accurately as possible according to the manufacturer's directions.

(d) The initial and final counter readings of the pump must be recorded. The sample volume can be obtained by multiplying the number of strokes by the volume/stroke factor.

(e) One charcoal tube should be treated in the same manner as the sample tubes (break, seal, ship), except that no air is drawn through it. This tube will serve as a blank.

Special Consideration

(a) Where two or more alkanes or other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be conveyed with the sample.

(b) The pump must not be operated for more than 8 hours without recharging the battery.

(c) If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, alkanes will not be trapped quantitatively. Therefore, in high humidity, the volume sampled should be reduced.

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

Shipping of Samples

Capped charcoal tubes should be packed tightly and padded before they are shipped to prevent tube breakage during shipping. Bulk samples of materials which may have been introduced into the workplace air and which may be collected by charcoal tubes must be submitted in addition to charcoal tubes. These bulk samples should be at least 20 ml each and should be refrigerated when practical. Bulk samples and charcoal tubes must be shipped in separate containers.

X. APPENDIX II

ANALYTICAL METHOD FOR ALKANES (C5-C8)

The following analytical method is adapted from the NIOSH/OSHA Standards Completion Program [61].

Principle of the Method

A known volume of air is drawn through a charcoal tube to collect alkane vapors.

Alkane vapors trapped on charcoal from a known volume of air are desorbed with carbon disulfide. An aliquot of the desorbed sample is injected into a gas chromatograph. The total area of the resulting peaks is determined and compared with those obtained from injection of alkane standards.

Range and Sensitivity

(a) The Standards Completion Program methods are valid over the concentration range of 800-7,000 mg/cu m at an atmospheric temperature of 25 C and a pressure of 760 mmHg for a 3-liter sample of the individual alkanes. Although not demonstrated, it is anticipated that this method will be valid for the concentration ranges specified in this document. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range of concentrations for each alkane analyzed.

(b) 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 the alkanes in the air.

Interference

Any compound which has about the same retention time as the alkanes under the gas-chromatographic conditions described in this method will interfere with the analysis. This type of interference might be overcome by changing the operating conditions of the instrument, the column, the column temperature, or all three. The interfering compounds can be identified by a combination of gas chromatography and mass spectrometry if interference is suspected. If the carbon disulfide interferes with components of a complex mixture, each sample may be analyzed on separate gas-chromatographic columns of widely different polarity. This will ensure that each component of the complex mixture can be analyzed in a region free of interference from carbon disulfide.

Advantages and Disadvantages of the Sampling and Analytical Methods

(a) The sampling device is small, portable, and involves no liquids. Samples are analyzed by means of a rapid instrumental method. The method provides for the simultaneous analysis of two or more compounds suspected to be present in a mixture by changing gas-chromatographic conditions from isothermal to a temperature-programmed mode of operation. Interferences may affect the qualitative and quantitative analysis of the compounds present in the sample. Mass spectrometry may be necessary to determine the identity of each compound present, if the alkane mixture being analyzed is complex. It may, however, not be able to provide an accurate quantitative analysis of the alkanes present in a complex mixture.

(b) The amount of sample which can be taken is limited by the amount that the charcoal tube will hold before it is overloaded. 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.

Apparatus

(a) Gas chromatograph equipped with flame ionization detector and mass spectrometer.

(b) Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW for operation above 50 C; column (10-ft x 1/8-in stainless steel) packed with 10% TCEP (triscyanoethoxy propane) on Chromosorb P-AW for operation below 50 C.

(c) Electronic integrator or some other suitable method of determining peak areas.

(d) Sample containers: 2 ml, with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

(e) Microliter syringes: 10-μl, and other convenient sizes for making standards.

(f) Pipets: 1.0 ml, graduated in 0.1-ml increments.

(g) Volumetric flasks: 10 ml or other convenient sizes for making standard solutions.

Reagents

(a) Chromatographic quality carbon disulfide.

(b) Samples of specific alkanes under study, preferably chromatoquality grade.

(c) Nonane or other suitable alkane for use as an internal standard.

(d) Purified compressed helium.

(e) Purified compressed hydrogen.

(f) Filtered compressed air.

Procedure

(a) Cleaning of Equipment

Wash all glassware used for the laboratory analysis with detergent in water, and thoroughly rinse with tapwater and distilled water.

(b) Analysis of Samples

(1) Preparation of samples: Score each charcoal tube with a file in front of the first section of charcoal, and break it open. Remove the glass wool and discard. Transfer the charcoal in the first (larger) section to a 2-ml stoppered sample container or to an automatic sample injector vial. Remove the separating section of foam and discard; transfer the second section to another sample container or vial. Analyze these two sections separately.

(2) Desorption of samples: Prior to analysis, pipet 1.0 ml of carbon disulfide into each sample container. For the internal standard method, use a 0.2% solution of internal standard in carbon disulfide. (Perform all work with carbon disulfide under a fume hood because of its high toxicity.) Desorb 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, cap the sample vials as soon as the solvent is added to minimize volatilization.

(3) Gas-chromatographic conditions: The typical operating conditions for the gas chromatograph are:

(A) 30 ml/minute (60 psig) helium carrier gas flow.

(B) 35 ml/minute (25 psig) hydrogen gas flow to detector.

(C) 400 ml/minute (60 psig) airflow to detector.

(D) 225 C injection port temperature.

(E) 250 C manifold temperature (detector).

(F) 52 C column (FFAP) temperature.

(4) Injection: The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, employ the solvent-flush injection technique. First, flush a 10-μl syringe with solvent several times to wet the barrel and plunger. Draw 3 μl of solvent into the syringe to increase the accuracy and reproducibility of the injected sample volume. Remove the needle from the solvent, and pull back the plunger about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. Immerse the needle in

the sample, and withdraw a 5-μl aliquot, 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, pull back the plunger 1.2 μl to minimize evaporation of the sample from the tip of the needle. Make certain that the sample occupies 4.9-5.0 μl in the barrel of the syringe. Make duplicate injections of each sample and standard. No more than a 3% difference in peak area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case, 2-μl injection volumes are satisfactory.

(5) Measurement of the peak area: Measure the area of the sample peak with an electronic integrator or by some other suitable means of area measurement, and read preliminary results from standard curves prepared as discussed below.

(c) Determination of Desorption Efficiency

(1) Importance of determination: The determined 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 that the same batch of charcoal is used.

(2) Procedure for determining desorption efficiency: Measure activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) into a 63.5 mm, 4-mm ID 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.

Inject a known amount of each alkane directly into the activated charcoal with a microliter syringe, and cap the tube. When using an automatic sample injector, sample injector vials, capped with inert polymer-faced septa, may be used instead of the glass tubes.

Prepare six tubes at each of three concentration levels (one-half, one, and two times the recommended limit) by adding an amount of each alkane equivalent to that which would be present in a 4-liter sample at the selected level. Allow the tubes to stand overnight to ensure complete adsorption of the alkanes onto the charcoal. These tubes are referred to as the samples. Treat a parallel blank tube in the same manner, except add no sample to it. Desorb and analyze the blank tubes in exactly the same manner as the sampling tube.

Prepare two or three standards 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 with 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{desorption efficiency} = \frac{\text{average weight recovered (mg)}}{\text{weight added (mg)}}$$

Plot the desorption efficiency versus the weight of each alkane added. This curve is used in calculations to correct for adsorption losses.

(d) Curves

It is convenient to express concentration of standards in terms of mg/1.0 ml of carbon disulfide because samples are desorbed in this amount of carbon disulfide. The density of each alkane is used to convert mg into microliters for easy measurement with a microliter syringe. A series of n-alkane standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas-chromatgrahic conditions and during the same time period as the unknown samples. When standards containing more than one n-alkane are blended, each component should be present in different relative amounts. Curves are established by plotting concentrations in mg/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 should be approximately 70% of the concentration at twice the environmental limit. The alkane concentration in mg/ml is plotted versus the area ratio of each alkane to that of the internal standard. Note: Whether the absolute area or the internal standard method is used, standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect of variations of flame ionization detector response.

Calculations

(a) The areas of peaks with retention times less than or equal to n-pentane are summed and converted to milligrams of pentane according to the n-pentane standard curve. The area of peaks with retention times greater than n-pentane but less than or equal to n-hexane are summed and converted to milligrams of hexane with the n-hexane standard curve. Heptanes and octanes are treated in a similar manner. For a homologous series of isomers, the flame ionization detector response factors are nearly the same as the parent alkane [119]. If a component can be demonstrated to be something other than an alkane, its area is not included. No volume corrections are needed, because the standard curves are based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

(b) 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.

(c) Read the desorption efficiency from the appropriate n-alkane curve for the amounts found in either the front or backup sections. Divide the total weight of the alkane by the desorption efficiency to obtain the corrected mg/sample.

$$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{desorption efficiency}}$$

(d) Add the corrected weights of the pentanes, hexanes, heptanes, and octanes present in the front and backup sections of the same sample tube to determine the total weight of the alkanes in the sample.

(e) The concentrations of alkanes in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg x 1,000 (liter/cu m)}}{\text{air volume sampled (liters)}}$$