XIII. APPENDIX IV

SAMPLING AND ANALYTICAL METHOD FOR VINYL BROMIDE IN AIR

The data presented in this proposed sampling and analytical method for vinyl bromide were adapted from NIOSH method No. P&CAM 127 for Organic Solvents in Air [336] and from information provided by Bales [249] and DW Yeager (written communication, February 1978). This proposed method, as outlined below, has not been tested by NIOSH but should allow routine analyses in the 1-ppm range.

Principle of the Method

(a) A known volume of air is drawn through a charcoal tube to trap the vinyl bromide present.

(b) The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

(c) An aliquot of the desorbed sample is injected into a gas chromatograph.

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

Range and Sensitivity

No data are currently available. However, Bales [249] reported measurement of vinyl bromide concentrations down to 0.01 ppm using this general method.

Interferences

(a) When the amount of water in the air is so great that condensation actually occurs in the tube, vinyl bromide will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

(b) It must be emphasized that any compound which has the same retention time as vinyl bromide at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

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

Precision and Accuracy

No data are currently available.

Advantages and Disadvantages of the Method

(a) 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 charcoal tubes are analyzed by means of a quick, instrumental method.

(b) One disadvantage of the method is that the amount of sample which can be taken is limited by the number of mg that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds approximately 20% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached.

(c) Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the two sections of the sampling tube. This drop will affect the flowrate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only. This disadvantage could be eliminated by calibrating the pump with a representative charcoal tube.

Apparatus

(a) An approved and calibrated personal sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter/minute or less.

(b) Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with a 6-mm outer diameter and a 4-mm inner diameter, containing two sections of 20/40-mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The 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 1 inch of mercury at a flowrate of 1 liter/minute.

(c) Gas chromatograph equipped with a flame-ionization detector.

(d) Column, 20 feet, SE-30. Other columns capable of performing the required separations may be used.

(e) A mechanical or electronic integrator or a recorder and some method for determining peak area.

(f) Glass stoppered micro tubes. The 2.5-ml graduated microcentrifuge tubes are recommended.

(g) Hamilton syringes: 10 µl, and convenient sizes for making standards.

(h) Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

(i) Volumetric flasks: 10 ml, or convenient sizes for making standard solutions.

Reagents

(a) Carbon disulfide, "spectroquality" or better.

(b) Sample of the specific compound under study, preferably "chromatoquality" grade.

(c) Helium, Bureau of Mines grade A.

(d) Prepurified hydrogen.

(e) Filtered, compressed air.

Procedure

(a) 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.

(b) Collection and Shipping of Samples

(1) Immediately before sampling, the ends of the charcoal tube should be broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

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

(3) The charcoal tube should be vertical during sampling.

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

(5) The flowrate, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flowrate of 1 liter/minute or less to attain the total sample volume required.

(6) The temperature and pressure of the atmosphere being sampled should be measured and recorded.

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

(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.

(9) Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

(10) Samples received at the laboratory are logged in and immediately stored in a refrigerator.

(c) Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

(d) Analysis of Samples

(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 small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

(2) Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each test tube and the glass stopper is inserted. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is agitated occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied

by the charcoal plus the 0.5 ml of carbon disulfide should be noted and corresponding volume adjustments should be made whenever necessary just before gas chromatographic analysis.

(3) Gas-Chromatographic Conditions. The typical operating conditions for the gas chromatograph are:

(A) 30 cc/minute helium carrier gas flow.

(B) 65 cc/minute (24 psig) hydrogen gas flow to detector.

(C) 500 cc/minute (50 psig) air flow to detector.

(D) 200 C injector temperature.

(E) 200 C manifold temperature (detector)

(F) Column temperature, 70 C, door on instrument closed.

(4) Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl 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 µl 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-µl 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 a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

(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.

(e) Determination of Desorption Efficiency

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

(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 5-cm, 4-mm inner diameter glass tube, flame-sealed at one end (similar to commercially available culture tubes). 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 vinyl bromide is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the vinyl bromide onto the charcoal. These five 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 Analysis of Samples.

Two or three standards are prepared by injecting the same volume of vinyl bromide into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the sample. These are anal Samplingyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or:

$$\text{Desorption Efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml of carbon disulfide because samples are desorbed in this amount of carbon disulfide. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the volume of vinyl bromide into 10 ml of carbon disulfide. For example, to prepare a 0.3 mg/0.5 ml of standard, one would inject 6.0 mg into exactly 10 ml of carbon disulfide in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into µl 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 gas-chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml vs peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the flame-ionization detector response.

Calculations

(a) The weight, in mg, corresponding to each peak area is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml of 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.

$$\text{Correct mg} = \text{mg(s)} - \text{mg(b)}$$

where:

mg(s) = mg found in front section of sample tube
mg(b) = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

(c) The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

(d) This total weight is divided by the determined desorption efficiency to obtain the total mg/sample.

(e) The volume of air sampled is converted to standard conditions of 25 C and 760 mmHg:

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

where:

Vs = volume of air in liters at 25 C and 760 mmHg
V = volume of air in liters as measured
P = barometric pressure in mmHg
T = temperature of air in degrees C

(f) The concentration of the vinyl bromide in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/liter of air:

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\text{total mg} \times 1{,}000\ (\mu\text{g/liter})}{Vs}$$

(g) Another method of expressing concentration is ppm:

$$ppm = \mu l \text{ of vinyl bromide}/Vs$$

$$ppm = \frac{\mu g \text{ of vinyl bromide}}{Vs} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25 C and 760 mmHg
MW = molecular weight of vinyl bromide

XIV. APPENDIX V

SAMPLING AND ANALYTICAL METHOD FOR VINYL FLUORIDE IN AIR

The data presented in this proposed sampling and analytical method for vinyl fluoride were adapted from NIOSH method No. P&CAM 127 for Organic Solvents in Air [336] and information provided by Bales [250] and DW Yeager (written communications, August 1977 and February 1978). The proposed method, as outlined below, has not been tested by NIOSH, but should allow routine analyses in the 1-ppm range.

Principle of the Method

(a) A known volume of air is pumped into a Teflon bag.

(b) An aliquot of the air sample in the bag is injected into a gas chromatograph.

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

Range and Sensitivity

The limit of detection has been reported as 1 ppm (1.88 mg/cu m) (DW Yeager, written communication, February 1978).

Interferences

(a) It must be emphasized that any compound which has the same retention time as vinyl fluoride at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

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

(c) If samples are not analyzed within 3-4 days, significant sample leakage may occur (DW Yeager, written communication, August 1977).

Precision and Accuracy

No data on precision and accuracy are available at this time.

Advantages and Disadvantages of the Method

(a) The sampling device is portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples are analyzed by means of a quick, instrumental method. No solvent desorption is necessary.

(b) One disadvantage of the method is that the amount of sample which can be taken is limited by the volume capacity of the bag. Full sample bags may interfere with the free movement of the worker.

(c) Furthermore, the precision of the method is limited by the reproducibility of the sampling rate of the pump.

Apparatus

(a) An approved and calibrated peristaltic sampling pump, diaphragm-pump, or vacuum pump, with filtered outlet to remove oil, for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter/minute or less.

(b) Teflon bag.

(c) Gas chromatograph equipped with a flame-ionization detector.

(d) Column, 20 feet, SE-30. Other columns capable of performing the required separations may be used.

(e) A mechanical or electronic integrator or a recorder and some method for determining peak area.

(f) Syringes: 5 ml.

Reagents

(a) Vinyl fluoride, 99%.

(b) Helium, Bureau of Mines grade A.

(c) Prepurified hydrogen.

(d) Filtered, compressed air.

Procedure

(a) Calibration of Personal Sampling Pumps. Each personal smapling pump must be calibrated with a representative bag in the line. This will minimize errors associated with uncertainties in the sample volume collected.

(b) Collection and Shipment of Samples

(1) The flowrate, time, and/or volume must be measured as accurately as possible. The sampling bags should be flushed before use. The sample should be taken at a flowrate of 1 liter/minute or less to attain the total sample volume required.

(2) The temperature and pressure of the atmosphere being sampled should be measured and recorded.

(3) Air samples are shipped to the laboratory for analysis in the Teflon bags. Appropriate precautions should be taken to prevent damage of the bags while in transit.

(c) Analysis of Samples

(1) Gas-Chromatographic Conditions. The typical operating conditions for the gas chromatograph are:

(A) 30 cc/minute helium carrier gas flow.

(B) 65 cc/minute (24 psig) hydrogen gas flow to detector.

(C) 500 cc/minute (50 psig) air flow to detector.

(D) 200 C injector temperature.

(E) 200 C manifold tempertaure (detector).

(F) Column temperature, 33 C, door of oven open and blower left on.

(2) Injection

Five milliliters of air from the Teflon bag is withdrawn with a syringe. Two milliliters are injected directly into the gas chromatograph.

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

Calibration and Standards

Standards are prepared by filling several Teflon bags with known concentrations of vinyl fluoride which cover the range of interest. Five milliliters of air from each standard bag are withdrawn and 2 ml are injected directly into the instrument.

Calibration curves are prepared by plotting the concentration (mg of vinyl fluoride/2 ml) vs peak area.

Calculations

(a) The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/2 ml and the volume of sample injected is identical to the volume of the standards injected.

(b) The volume of air sampled (collected in bag) is converted to standard conditions of 25 C and 760 mmHg:

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

where:

Vs = volume of air in liters at 25 C and 760 mmHg
V = volume of air in liters as measured
P = barometric pressure in mmHg
T = temperature of air in degrees centigrade

(c) The concentration of vinyl fluoride in the air sampled can be expressed in mg/cu m, which is numerically equal to μg/liter of air:

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\text{total mg} \times 1{,}000\ (\mu\text{g/mg})}{Vs}$$

XV. APPENDIX VI

SAMPLING AND ANALYTICAL METHOD FOR VINYLIDENE FLUORIDE IN AIR

The data presented in this proposed sampling and analytical method for vinylidene fluoride were adapted from NIOSH method No. P&CAM 127 for Organic Solvents in Air [336] and from information provided by the Pennwalt Corporation [251] and JL Sadenwasser (written communication, March 1978). This proposed method, as outlined below, has not been tested by NIOSH, but it should allow routine analyses in the 1-ppm range.

Principle of the Method

(a) A known volume of air is drawn through two charcoal tubes in series to trap the vinylidene fluoride present.

(b) The charcoal in the tubes is transferred to a small, graduated test tube and desorbed with carbon disulfide.

(c) An aliquot of the desorbed sample is injected into a gas chromatograph.

(d) The area of the resulting peak is determined and compared with areas obtained from the injection of standards

Range and Sensitivity

No data are currently available. However, Sadenwasser (written communication, March 1978) reported measuring vinylidene fluoride concentrations down to about 2 ppm using this general method.

Interferences

(a) When the amount of water in the air is so great that condensation actually occurs in the tube, vinylidene fluoride will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

(b) It must be emphasized that any compound which has the same retention time as vinylidene fluoride at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical

identity. For this reason it is important that a sample of the solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

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

(d) If samples are not analyzed within 5 days, significant sample loss may occur. Although no specific data were provided, JL Sadenwasser (written communication, March 1978) stated that vinylidene fluoride was retained by the charcoal for at least 5 days with little loss.

Precision and Accuracy

No data are currently available.

Advantages and Disadvantages of the Method

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

(b) One disadvantage of the method is that the amount of sample which can be taken is limited by the number of mg that the tubes will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds approximately 20% of that found on the front section, the possibility of sample loss exists. Sampling at 1 liter/minute caused a significant breakthrough after collection of 3 liters. During sample storage, volatile compounds such as vinylidene fluoride will migrate throughout the tube until equilibrium is reached.

(c) Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the two sections of the sampling tubes. This drop will affect the flowrate and cause the volume to be imprecise, because the pump is usually calibrated for one particular tube only. This disadvantage could be eliminated by calibrating the pump with representative charcoal tubes.

Apparatus

(a) An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 0.5 liter/minute or less.

(b) Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with a 6-mm outer diameter and a 4-mm inner diameter, containing two sections of 20/40-mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The 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 1 inch of mercury at a flowrate of 1 liter/minute.

(c) Gas chromatograph equipped with a flame-ionization detector.

(d) Column, stainless steel, 6-feet x 1/8-inch outer diameter, packed with Chromosorb 102, 80/100 mesh. Other columns capable of performing the required separations may be used.

(e) A mechanical or electronic integrator or a recorder and some method for determining peak area.

(f) Glass stoppered micro tubes. The 2.5-ml graduated microcentrifuge tubes are recommended.

(g) Hamilton syringes: 10 µl, and convenient sizes for making standards.

(h) Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1 ml increments.

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

Reagents

(a) Carbon disulfide, "spectroquality" or better.

(b) Sample of the specific compound under study, preferably "chromatoquality" grade.

(c) Helium, Bureau of Mines grade A.

(d) Prepurified hydrogen.

(e) Filtered, compressed air.

Procedure

(a) Calibration of Personal Sampling Pumps. Each personal sampling pump

must be calibrated with representative charcoal tubes in the line. This will minimize errors associated with uncertainties in the sample volume collected.

(b) Collection and Shipping of Samples

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

(2) Position the second charcoal tube next to the sampling pump in tandem with the first tube, to serve as a backup. If one tube is used the smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

(3) The charcoal tube should be vertical during sampling.

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

(5) The flowrate, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flowrate of 0.5 liter/minute or less to attain the total sample volume required. The sensitivity of the method is increased by using lower flowrates to increase the amount of sample collected (JL Sademwasser, written communication, March 1978).

(6) The temperature and pressure of the atmosphere being sampled should be measured and recorded.

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

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

(9) Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

(10) Samples received at the laboratory are logged in and immediately stored in a refrigerator.

(c) Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

(d) Analysis of Samples

(1) Preparation of Samples. The two tubes used in the collection of

a single sample are analyzed separately. If only one tube is used for sampling, then each section of activated carbon should be analyzed separately. 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 small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

(2) Desorption of Samples. Prior to analysis, 2 ml of carbon disulfide is pipetted into each test tube and the glass stopper is inserted. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 15 minutes if the sample is agitated occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 2 ml of carbon disulfide should be noted and corresponding volume adjustments should be made whenever necessary just before gas-chromatographic analysis.

(3) Gas-Chromatographic Conditions. The typical operating conditions for the gas chromatograph are:

(A) 30 cc/minute helium carrier gas flow.

(B) 50 cc/minute (24 psig) hydrogen gas flow to detector.

(C) 500 cc/minute (50 psig) air flow to detector.

(D) 150 C injector temperature.

(E) 200 C manifold temperature (detector)

(F) Column temperature, 100 C, door on instrument closed.

(4) Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-μl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 1-μl 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 a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. A larger sample injection may be used to increase the sensitivity of the method (JL Sadenwasser, written communication, March 1978).

(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.

(e) Determination of Desorption Efficiency

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

(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 5-cm, 4-mm inner diameter glass tube, flame-sealed at one end (similar to commercially available culture tubes). 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 vinylidene fluoride is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the vinylidene fluoride onto the charcoal. These five 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 Analysis of Samples.

Two or three standards are prepared by injecting the same volume of vinylidene fluoride into 2 ml of carbon disulfide with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or:

$$\text{Desorption Efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

Calibration and Standards

It is convenient to express concentration of standards in terms of mg/2 ml of carbon disulfide because samples are desorbed in this amount of carbon disulfide. To minimize error due to the volatility of carbon disulfide, one can inject five times the volume of vinylidene fluoride into 10 ml of carbon disulfide. For example, to prepare 0.3 mg/2 ml of standard, one would inject 1.5 mg into exactly 10 ml of carbon disulfide in a glass-stoppered flask. The density of the specific compound is used to convert 1.5 mg into µl 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 gas-chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/2 ml vs peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the flame-ionization detector response.

Calculations

(a) The weight, in mg, corresponding to each peak area is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg/2 ml of 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:

$$\text{Correct mg} = \text{mg(s)} - \text{mg(b)}$$

where:

mg(s) = mg found in front section of sample tube
mg(b) = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

(c) The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

(d) This total weight is divided by the determined desorption efficiency to obtain the total mg/sample.

(e) The volume of air sampled is converted to standard conditions of 25 C and 760 mmHg:

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

where:

Vs = volume of air in liters at 25 C and 760 mmHg
V = volume of air in liters as measured
P = barometric pressure in mmHg
T = temperature of air in degrees C

(f) The concentration of the vinylidene fluoride in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/liter of air:

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\text{total mg} \times 1{,}000\ (\mu\text{g/mg})}{Vs}$$

(g) Another method of expressing concentration is ppm:

$$\text{ppm} = \mu\text{l of vinylidene fluoride}/Vs$$

$$\text{ppm} = \frac{\mu\text{g of vinylidene fluoride}}{Vs} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25 C and 760 mmHg
MW = molecular weight of vinylidene fluoride