

VII. REFERENCES

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VIII. APPENDIX I
SAMPLING AND ANALYTICAL PROCEDURES
FOR DETERMINATION OF CHLOROFORM

Atmospheric Sampling

(a) General Requirements

(1) The measurement of air concentrations shall be within the breathing zone of workers and shall meet the following criteria in order to evaluate conformance with the standard:

(2) Samples collected shall be representative of exposure of individual workers.

(3) Sampling data sheets shall include a log of:

(A) The date and time of sample collection

(B) Sampling duration

(C) Total sample volume

(D) A description of the sampling location

(E) Temperature, pressure, and relative humidity

at time of sampling

(F) Other pertinent information

(b) Breathing Zone Sampling

(1) Breathing zone samples shall be collected as near as practicable to the face of workers without interfering with freedom of movement and shall characterize the exposure from each job or specific operation in each production area.

(2) An approved, calibrated, battery-operated personal sampling pump plus an activated charcoal tube shall be used to collect the sample.

(3) The activated charcoal tube shall be attached to the clothing of the worker; the shirt collar is convenient for this purpose.

(4) Breathing zone samples shall be collected to permit determination of TWA workday exposures for every job involving exposure to chloroform in sufficient numbers to express the variability of the work situation. The minimum number of TWA's to be determined is listed in Section 7 of this standard, according to the number of employees involved.

(c) Apparatus

(1) Pump, battery-operated, complete with clip for attachment to the worker or a reliable, calibrated hand pump. All pumps and flowmeters must be calibrated with a representative charcoal tube in the line.

(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 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 glass wool is placed in front of the absorbing section. The pressure drop across the tube when in use must be less than 1 inch of mercury at a flowrate of 1 liter/min.

(d) Calibration of Sampling Instruments

(1) Air sampling instruments shall be calibrated with a representative charcoal tube in line, over a normal range of flowrates (50-

1000 ml/min) and pressure drops. Calibration curves shall be established for each sampling pump and shall be used in adjusting the pump prior to field use. Also calibration curves shall be established for each sampling pump after making any repairs or modifications to the sampling system.

(2) The volumetric flowrate through the sampling system shall be spot-checked and the proper adjustments made before and during each study to ensure obtaining accurate airflow data.

(e) Collection and Handling of Samples

(1) Immediately before sampling, break both ends of the tube to provide openings at least one-half the internal diameter of the tube (2mm).

(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 placed in a vertical position during sampling with the inlet facing down.

(4) Tubing may be used to connect the back of the tube to the pump, but air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

(5) The flowrates, sampling time involved and/or the total volume of air sampled must be measured accurately. The sample can be taken at flow rates of 50-1000 ml/min. Total sample volumes of 1-30 liters are recommended. It is also recommended that the sampling be less than 4 hours.

(6) Measure and record the temperature and pressure of the atmosphere being sampled.

(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 charcoal 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 after sampling to minimize tube breakage during transport.

(10) Charcoal tubes should be shipped separately from bulk samples.

Sample Analysis

(a) Principle of the Method

(1) A known volume of air is drawn through a charcoal tube to trap the chloroform vapor.

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

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

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

(b) Range and Sensitivity

(1) The lower limit for detection of chloroform at a 16 x 1 attenuation on a gas chromatograph with a 10:1 splitter is 0.10 mg/sample. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

(2) The upper limit value for chloroform is 2.0 mg/sample. This is the estimated amount of chloroform which the front section will hold before this compound is found on the backup section. If a particular atmosphere is suspected of containing a large amount of chloroform, it is recommended that a smaller sample volume be taken.

(c) Interferences

(1) When the amount of water in the air is so great that condensation actually occurs in the tube, chloroform will not be trapped.

(2) Any compound which has the same retention time as chloroform at the operating conditions described in this method could be an interference.

(d) Advantages of the Method

(1) This method is advantageous in that it provides one basic method for determining many different organic compounds.

(2) The sampling device is small, portable, and involves no liquids.

(3) Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions.

(4) The analysis of the tubes is accomplished by using a quick instrumental method.

(e) Disadvantages of the Method

(1) The amount of sample which can be taken is limited by the weight of chloroform which the tube will hold before overloading.

(2) When the sample value obtained for the backup section of charcoal exceeds 25% of that found on the front section, the possibility of appreciable sample loss exists.

(3) Other chlorinated hydrocarbons may displace chloroform from the charcoal.

(f) Apparatus

(1) Gas chromatograph equipped with a flame ionization detector.

(2) Stainless steel column (20 ft x 1/8 in) with 10% free fatty acid polymer (FFAP) stationary phase on 80/100 mesh, acid washed dimethyldichlorosilane (DMCS) treated Chromosorb W (or equivalent) solid support.

(3) A recorder and some method for determining peak area.

(4) Glass stoppered microtubes. The 2.5-ml graduated microcentrifuge tubes are recommended.

(5) Microsyringe of 10- μ l capacity, and convenient sizes for making standards.

(6) Pipets. 0.5-ml delivery pipets or 1.0-ml graduated pipets in 0.1-ml increments.

(7) Volumetric flasks of 10-ml capacity or convenient sizes for making standard solutions.

(g) Reagents

(1) Spectroquality carbon disulfide

(2) CHCl₃, preferably chromatography grade

(3) Bureau of Mines Grade A helium

(4) Prepurified hydrogen

(5) Filtered compressed air

(h) Procedure

(1) All equipment used for the laboratory analysis should be washed in detergent followed by tap and distilled water rinses.

(2) Preparation of samples

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 foam is removed and discarded; the second section is transferred to another test tube. These 2 sections are analyzed separately.

(3) Desorption of Samples

Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each test tube. ALL WORK WITH CARBON DISULFIDE SHOULD BE PERFORMED UNDER A HOOD BECAUSE OF ITS HIGH TOXICITY AND ITS FLAMMABILITY. Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 ml carbon disulfide should be noted and corresponding volume adjustments should be made whenever necessary just before analysis.

(4) Gas chromatographic conditions

Operating conditions for a typical gas chromatograph are:

(A) 85 cc/min (70 psig) helium carrier gas flow

(B) 65 cc/min (24 psig) hydrogen gas flow to

detector

- (C) 500 cc/min (50 psig) airflow to detector
- (D) 200 C injector temperature
- (E) 200 C manifold temperature (detector)
- (F) Oven temperature 80 C isothermal

(5) 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, the solvent flush injection technique is employed. The 10- μ l syringe is first flushed with carbon disulfide several times to wet the barrel and plunger. Three μ l of carbon disulfide are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the carbon disulfide solvent, and the plunger is pulled back about 0.2- μ l 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- μ l 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.

(6) Measurement of Area

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

(7) Calibration and Standards

(A) Preparation of Standards

It is convenient to prepare standards in terms of mg chloroform per 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, 20 times the weight can be injected into 10 ml of carbon disulfide. For example, to prepare a 0.3 mg/0.5 ml standard, 6.0 mg is injected into exactly 10 ml of carbon disulfide in a glass stoppered flask. The density for chloroform is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards are prepared, varying in concentration over the range of interest and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration versus average peak area.

(B) Determination of Desorption Efficiency

It is necessary to determine the percentage of chloroform on the charcoal that is removed in the desorption process. This desorption efficiency is determined once for a given compound provided the same batch of charcoal is always used.

Activated charcoal, equivalent to the amount in the first section of the sampling tube (100 mg), is measured into a 2-inch long tube, with an inside diameter of 4 mm, 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 compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more parafilm.

At least 5 tubes are prepared in this manner and allowed to stand at least overnight to assure complete adsorption of chloroform onto the charcoal. These 5 tubes will be referred to as the "desorption samples". A parallel blank tube should be treated in the same manner except that no chloroform is added to it. The desorption sample and blank tubes are desorbed and analyzed in exactly the same manner as previously described.

Two or 3 desorption standards are prepared for analysis by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the desorption sample. These are analyzed with the desorption samples.

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

$$\text{desorption efficiency} = \frac{\text{Desorption sample area} - \text{Blank area}}{\text{Desorption standard area}}$$

Sample Calculations

(a) Read the weight of chloroform corresponding to the peak area for chloroform from the standard curve. No volume corrections are needed because the standard curve is based on mg CHCl_3 /0.5 ml carbon disulfide, and the volume of sample injected is identical to the volume of the standards injected.

(b) Separately determine the weights of chloroform on the front and backup sections of the charcoal tube.

(c) Corrections must be made to the chloroform weights determined on both the front and backup sections for the weights of the respective sections of the blank charcoal tube.

(1) Subtract the weight of chloroform found on the front section of the blank charcoal tube from the weight of chloroform found on the front section of the sample charcoal tube to give a corrected front section weight.

(2) Subtract the weight of chloroform found on the backup section of the blank charcoal tube from the weight of chloroform found on the backup section of the sample charcoal tube to give a corrected backup section weight.

(3) Add the corrected amounts of chloroform present on the front and backup sections of the sample tube to determine the total measured chloroform in the sample.

(4) Divide this total weight by the determined desorption efficiency to obtain M, the total mg per sample.

(d) Convert the liters of air sampled (V) to volume (V') at standard conditions of 25 C and 760 mm Hg, as follows:

$$V' = \frac{298VP}{760 (T+273)}$$

Where:

V' = volume of air in liters at 25 C and 760 mm Hg

V = measured volume of air in liters sampled

P = barometric pressure in mm Hg at time of
sampling measured

T = temperature of air in degree centigrade at time
of sampling measured

(e) The concentration of chloroform in the sampled air can be expressed in various ways using M , the weight of chloroform obtained in (c)(4) and V' , the standardized sample volume, obtained in (d), as follow:

$$(1) \quad \mu\text{g/liter} = 1000 M/V'$$

$$(2) \quad \text{mg/cu m} = 1000 M/V'$$

$$(3) \quad \text{ppm} = 205 M/V'$$