

## VI. WORK PRACTICES

The 2 methods currently used for manufacturing carbon tetrachloride are the chlorination of methane and the chlorination of carbon disulfide. Suitable controls for the safe use of methane, chlorine, and carbon disulfide should be used.

Information about engineering controls for the handling of chlorine and carbon disulfide is given in the respective Chemical Safety Data Sheets of the Manufacturing Chemists' Association. [139,140] The Manufacturing Chemists' Association's Safety Data Sheet, SD-3 [1] provides further information concerning specific work practices for carbon tetrachloride.

### (a) Bulk Handling

All piping and valves at the unloading station should be carefully inspected prior to connection to the transport vehicle. Personal protection must be provided during both inspection and connection. Periodic inspection during unloading is also recommended to avoid the possibility of leaks. Eye wash and safety shower installations should be readily available in the immediate area. In cold climates these installations may be located just inside an easily accessible door of a building. All personnel involved in unloading must be made aware of the toxic properties of the solvent and the necessity for wearing the proper personal protection. Unloading areas must be properly posted "Danger: unloading carbon tetrachloride". The wheels of the tank trucks must be chocked. A metal rail-mounted flag and derailler must be mounted between the tank car and incoming rail traffic. Pipes, pumps, and related equipment must be labeled as containing carbon tetrachloride.

(b) Storage and Use

Carbon tetrachloride should be stored in cool, dry places. It is corrosive to iron and certain other metals when in contact with water, especially at elevated temperatures and reacts violently with aluminum and magnesium. Vessels and equipment which will contain carbon tetrachloride should be of tin, galvanized iron, nickel or nickel-copper alloys, or of especially resistive lined containers. [1,2]

The processes in which carbon tetrachloride is used should be in closed systems whenever feasible. Vents on tanks or vessels must be provided where large volumes of carbon tetrachloride are used or stored. A scrubber should be installed in the venting system to prevent carbon tetrachloride vapor from escaping to the outside atmosphere. All outside exhaust vents must be posted and located away from any location where people normally work. All piping and equipment should be marked as containing carbon tetrachloride. Piping should be located so that the possibility of mechanical damage to it is minimized.

Safety showers and eye wash facilities are necessary in areas where accidental exposure is likely to occur. Use of these facilities minimizes the effects of skin and eye exposure prior to medical or first aid treatment. Recording of the incident at the time of treatment is important for future reference should the incident result in adverse health effects.

(c) Equipment Maintenance

All equipment used for handling carbon tetrachloride must be emptied and purged prior to entry or disassembly. Tanks may only be entered after it has been determined that the level of carbon tetrachloride is within acceptable limits and that the oxygen content is adequate (20%). Emergency

entry may be made only if a self-contained breathing unit is provided and protective clothing is worn.

(d) Emergencies

Spills must be anticipated. Storage tanks should be diked to contain the contents of the tank. Areas where major spills are likely to occur should be constructed so that they may be closed until properly protected personnel can enter, clear, and ventilate the area. Normal work should not be continued until the exposure level has been reduced to the level prescribed by this standard. Disposal of carbon tetrachloride or carbon tetrachloride contaminated materials should be done in compliance with local, state, and federal regulations. Consideration should be given to pumping the diked spill to another tank. In addition, it is advisable to have facilities for transfer of the contents of a leaking tank to another suitable tank.

Maintenance personnel involved in emergency rescue or cleanup must be informed of the toxic properties of the solvent and instructed on the necessity of wearing personal protective equipment.

(e) Skin and Eye Protection

Carbon tetrachloride is irritating to the skin, [13,25] and can also be absorbed by this route. [22,48] For these reasons, protective clothing that is both resistant and relatively impervious to carbon tetrachloride should be used whenever liquid carbon tetrachloride is handled. Information about penetration of carbon tetrachloride through some materials can be found in the report by Johnson and Merciez. [141] Additional information about penetration of carbon tetrachloride through various materials and also their resistance to breakdown by carbon

tetrachloride can be found in Rogers' report. [142] Carbon tetrachloride liquid and vapor can affect the eye, [13,25,27,28,56,58] and chemical type goggles made entirely of carbon tetrachloride resistant materials should be used wherever there is work with liquid carbon tetrachloride.

(f) Respiratory Protection

For adequate respiratory protection against the conditions which may be encountered in individual operations, many types of respirators have been developed and approved. Each has a particular field of application and limitations from the viewpoint of protection, as well as advantages and disadvantages from the viewpoint of operational procedures and maintenance. Detailed information on the selection and use of respirators can be obtained from the Respiratory Protective Devices Manual [143] published by the AIHA and the ACGIH in 1963. The American National Standards Practices for Respiratory Protection, ANSI Z88.2-1969, [144] also classifies, describes, and gives the limitations of respirators.

There are 3 categories of respirators: atmosphere-supplying respirators, air-purifying respirators, and the combination of atmosphere-supplying and air-purifying respirators.

One factor that affects the overall performance of demand type (negative pressure) respirators is the variability of the face seal. Facepiece leakage is the major limitation of half-mask and quarter-mask facepieces operated with a negative pressure.

For purposes of uniform regulations covering the many face sizes and shapes of the US population, NIOSH recommends that the half-mask or quarter-mask facepieces operated with a negative pressure not be used for protection above 10 times the TWA, although the majority of wearers can

obtain protection in atmospheres of higher carbon tetrachloride concentrations. On the same basis, NIOSH recommends that the full facepiece, operated with negative pressure, may be used up to 50 times the TWA.

Carbon tetrachloride, with an odor threshold above 20 ppm, [145,146] has poor warning properties and air-purifying respirators are not recommended.

NIOSH periodically issues a list of approved or certified respiratory protective devices. All devices approved by the Bureau of Mines are listed in Information Circular 8559 and supplements. All types of devices certified by the Testing and Certification Laboratory of NIOSH are listed in a separate publication. These are available from the Testing and Certification Laboratory, NIOSH, Morgantown, West Virginia 26505.

## VII. REFERENCES

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VIII. APPENDIX I  
SAMPLING PROCEDURE FOR  
COLLECTION OF CARBON TETRACHLORIDE

General Requirements

(a) Air samples representative of the breathing zone of workers shall be collected to characterize the exposure from each job or specific operation in each work area.

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

(c) A record shall be made of:

(1) The date and time of sample collection.

(2) Sampling duration.

(3) Total sample volume.

(4) Location of sampling.

(5) Temperature, pressure, and relative humidity at time of sampling.

(6) Other pertinent information.

Sampling

(a) Samples shall be collected as near as practicable to the face of workers without interfering with freedom of movement.

(b) Samples shall be collected to permit determination of TWA workday exposures for every job involving exposure to carbon tetrachloride in sufficient numbers to express the variability of the exposures for the

work situation. The minimum numbers of TWA's to be determined are listed in Section 7 of the recommended standard, according to the number of employees involved.

(c) Apparatus for Charcoal Tube Sampling

(1) Pump, battery-operated, complete with clip for attachment to the worker. Airflow through the pump shall be within  $\pm 5\%$  of the desired rate.

(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 coconut-shell charcoal separated by a 2-mm portion of urethane foam. The first is the adsorbing section and contains 100 mg of charcoal from coconut shells. The second, or reserve section, contains 50 mg. A 3-mm portion of urethane foam is placed between the outlet of the tube and the reserve section. A plug of glass wool is placed in front of the adsorbing 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). Calibration curves shall be established for each sampling pump and shall be used in adjusting the pump prior to and during each field use. New 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 (2 mm).

(2) The smaller section of charcoal is used as a reserve 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 sample can be taken at flowrates of 50-1,000 ml/min, depending on the pump. Total sample volumes of 5-80 liters are recommended, eg, a sample could be collected at 1,000 ml/min for 80 minutes to give a total sample volume of 80 liters, or at 50 ml/min for 10 hours to give a total sample volume of 30 liters. However, it is also recommended that each sample be collected in less than 4 hours.

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

(7) One charcoal tube, to serve as an analytical blank, should be handled in the same manner as the sample tube (break, seal, and transport) except that no air is sampled through this tube.

IX. APPENDIX II  
ANALYTICAL PROCEDURE FOR DETERMINATION OF  
CARBON TETRACHLORIDE

Principle of the Method

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

(b) The carbon tetrachloride is desorbed from the charcoal 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

(a) The lower limit for detection of carbon tetrachloride on a gas chromatograph with a flame ionization detector is 5  $\mu\text{g}/\text{sample}$ .

(b) The upper limit value for carbon tetrachloride is 1.0 mg/sample. This is the estimated amount of carbon tetrachloride which the front section will hold before this compound breaks through to the reserve section of charcoal. If a particular atmosphere is suspected of containing a large amount of carbon tetrachloride, it is recommended that a smaller volume of air be sampled.

### Interferences

(a) Carbon tetrachloride will not be trapped when the amount of water in the air is so great that condensation occurs in the charcoal sampling tube.

(b) Any compound which has the same retention time as carbon tetrachloride with the chromatographic conditions described in this method could interfere. These may be eliminated by altering operating conditions of the gas chromatograph using a different column packing or using a selective detector, ie, electron capture.

### Advantages of the Method

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

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

(c) The analysis of the tubes can be accomplished rapidly.

### Disadvantages of the Method

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

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

(c) Other organic compounds in high concentrations may displace carbon tetrachloride from the charcoal.

### Apparatus

- (a) Gas chromatograph equipped with a flame ionization detector.
- (b) Stainless steel column (20 ft x 1/8 in) with 10% free fatty acid polymer (FFAP) stationary phase on 80/100 mesh Chromosorb W (or equivalent), acid washed and treated with dimethyldichlorosilane.
- (c) A recorder and some method for determining peak area.
- (d) Glass stoppered microtubes of 2.5-ml capacity or 2-ml vials that can be sealed with inert caps.
- (e) Microsyringe of 10- $\mu$ l capacity, and convenient sizes for making standards.
- (f) Pipets. 0.5-ml delivery pipets or 1.0-ml pipets graduated in 0.1-ml increments.
- (g) Volumetric flasks of 10-ml capacity or convenient sizes for making standard solutions.

### Reagents

- (a) Spectroquality carbon disulfide.
- (b) Carbon tetrachloride, preferably chromatquality grade.
- (c) Bureau of Mines Grade A Helium.
- (d) Prepurified hydrogen.
- (e) Filtered compressed air.

### Analysis of Samples

- (a) All equipment used in the analysis should be washed in detergent followed by appropriate tap and distilled water rinses.

(b) Preparation: 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 similar test tube. These 2 sections are analyzed separately.

(c) Desorption: Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each test tube to desorb carbon tetrachloride from the charcoal.

EXTREME CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING CARBON DISFULIDE BECAUSE OF ITS HIGH TOXICITY AND FIRE AND EXPLOSION HAZARDS. IT CAN BE IGNITED BY HOT STEAM PIPES. ALL WORK WITH CARBON DISULFIDE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

(d) Typical chromatographic operating conditions:

- (1) 50 ml/min (70 psig) helium carrier gas flow.
- (2) 65 ml/min (24 psig) hydrogen gas flow to detector.
- (3) 500 ml/min (50 psig) airflow to detector.
- (4) 200 C injector temperature.
- (5) 200 C manifold temperature (detector).
- (6) 60 C isothermal oven or column temperature.

(e) 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- $\mu$ l syringe is first flushed with carbon disulfide several times to wet the barrel and plunger. Three  $\mu$ 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 $\mu$ 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- $\mu$ 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.

(f) Measurement of area: The area of the sample peak is determined and preliminary sample results are read from a standard curve prepared as discussed below.

#### Determination of Desorption Efficiency

It is necessary to determine the percentage of carbon tetrachloride 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 inert plastic. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with inert plastic.

At least 5 tubes are prepared in this manner and allowed to stand at least overnight to ensure complete adsorption of carbon tetrachloride 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 carbon tetrachloride is added to it. The desorption samples and blanks 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 carbon tetrachloride into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the desorption samples. 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

$$\text{desorption efficiency} = \frac{\text{area of sample} - \text{area of blank}}{\text{area of standard}}$$

#### Calibration and Standards

It is convenient to prepare standards in terms of mg carbon tetrachloride 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 of carbon tetrachloride is injected into exactly 10 ml of carbon disulfide in a glass-stoppered flask. The density of carbon tetrachloride (1.59 g/ml) is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards is 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.

#### Calculations

(a) The weight in mg corresponding to the peak area is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg carbon tetrachloride/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 carbon tetrachloride on the front and reserve sections of the charcoal tube.

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

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

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

(3) Add the corrected amounts of carbon tetrachloride present on the front and reserve sections of the sample tube to determine the total measured carbon tetrachloride 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 sampled air in liters at 25 C and 760 mm Hg

V = measured volume of sampled air in liters

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

T = temperature of air in degree Celsius, measured at time of sampling

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

(1)  $\text{mg/liter} = M/V'$

(2)  $\text{mg/cu m} = \mu\text{g/liter} = 1,000 M/V'$

(3)  $\text{ppm} = 159 M/V'$