

IX. APPENDIX I  
SAMPLING PROCEDURES  
FOR COLLECTION OF 1,1,1-TRICHLOROETHANE

General Requirements

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

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

(c) Suggested records:

- (1) The date and time of sample collection.
- (2) Sampling rate and 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 should be collected as near as practicable to the faces of workers without interfering with freedom of movement.

(b) Samples should be collected to permit determination of TWA workday and ceiling exposures for every job involving exposure to 1,1,1-trichloroethane in sufficient numbers to express the variability of the exposures for the work situation.

(c) Apparatus for Charcoal Tube Sampling

(1) Pump, battery-operated, complete with clip for attachment to the worker.

(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 two sections of 20/40 mesh activated coconut-shell charcoal, fired at 600 C, 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 silitated 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 should be calibrated with a representative charcoal tube in line, over a normal range of flowrates (25-1000 ml/min). Calibration curves must be established for each sampling pump and be used in adjusting the pump prior to and during each field use. Airflow through the pump should be within  $\pm 5\%$  the desired rate. New calibration curves should be established for each sampling pump after making any repairs or modifications to the sampling system.

(2) The volumetric flowrate through the sampling system should 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, to prevent channeling which would result in sample loss.

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

(5) The sample can be taken at flowrates of 25-1000 ml/min, depending on the pump. Total sample volumes of less than 35 liters are recommended, eg, a sample could be collected at 200 ml/min for 15 minutes to give a total sample of 3 liters, or at 25 ml/min for 24 hours to give a total sample volume of 36 liters. However, for determining the action level, it is also recommended that each sample be collected in 4 hours or less.

(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 passed through this tube.

X. APPENDIX II - ANALYTICAL PROCEDURES FOR DETERMINATION  
OF 1,1,1-TRICHLOROETHANE

Principle of the Method

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

(b) The 1,1,1-trichloroethane 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 1,1,1-trichloroethane on a gas chromatograph with a flame ionization detector is 300 ng/sample.

(b) The upper limit value for 1,1,1-trichloroethane is 36.0 mg/sample. This is the estimated amount of 1,1,1-trichloroethane 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 high concentration of 1,1,1-trichloroethane, it is recommended that a smaller volume of air be sampled.

### Interferences

(a) 1,1,1-Trichloroethane 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 1,1,1-trichloroethane with the chromatographic conditions described in this method could interfere. Such interferences may be eliminated by altering operating conditions of the gas chromatograph using a different column packing or using a selective detector.

### Advantages of the Method

(a) This method provides one basic procedure 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 1,1,1-trichloroethane 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 1,1,1-trichloroethane 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 (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) 1,1,1-Trichloroethane, preferably "chromatoquality" grade.
- (c) Bureau of Mines Grade A helium or nitrogen.
- (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 vial. The separating foam is removed and discarded; the second section is transferred to another similar test tube. These two sections are analyzed separately. Prior to analysis, 0.5 ml of carbon disulfide is pipetted (not by mouth) into each test tube to desorb 1,1,1-trichloroethane from the charcoal. A desorption time of 30 minutes, with occasional stirring, is recommended.

EXTREME CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING CARBON DISULFIDE 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.

(c) 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.

(d) 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 microliters 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 portion 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.

(e) 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 1,1,1-trichloroethane 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 I.D. 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 five tubes are prepared in this manner and allowed to stand at least overnight to ensure complete adsorption of 1,1,1-trichloroethane onto the charcoal. These five tubes will be referred to as the "desorption samples." A parallel blank tube should be treated in the same manner except that no 1,1,1-trichloroethane is added to it. The desorption samples and blanks are desorbed and analyzed in exactly the same manner as previously described.

Two or three desorption standards are prepared for analysis by injecting the same volume of 1,1,1-trichloroethane 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 1,1,1-

trichloroethane/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 1,1,1-trichloroethane is injected into exactly 10 ml of carbon disulfide in a glass-stoppered flask. The density of 1,1,1-trichloroethane (1.2528 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 1,1,1-trichloroethane/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 1,1,1-trichloroethane on the front and reserve sections of the charcoal tube.

(c) Corrections must be made to the 1,1,1-trichloroethane 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 1,1,1-trichloroethane found on the front section of the blank charcoal tube from the weight of 1,1,1-

trichloroethane found on the front section of the sample charcoal tube to give a corrected front section weight.

(2) Subtract the weight of 1,1,1-trichloroethane found on the reserve section of the blank charcoal tube from the weight of 1,1,1-trichloroethane found on the reserve section of the sample charcoal tube to give a corrected reserve section weight.

(3) Add the corrected amounts of 1,1,1-trichloroethane present on the front and reserve sections of the sample tube to determine the total measured 1,1,1-trichloroethane 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:

$$V' = \frac{298VP}{760(T+273)} = \frac{0.392VP}{(T+273)}$$

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 1,1,1-trichloroethane in the sampled air can be expressed in various ways using M, the weight of 1,1,1-trichloroethane obtained in (c)(4), and V', the standardized sample volume, obtained in (d), as follows:

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

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

(3)  $\text{ppm} = 247 \text{ M/V}'$

XI. APPENDIX III  
MATERIAL SAFETY DATA SHEET

General instructions for preparing a Material Safety Data Sheet (MSDS) are presented in this chapter. The examples used in the text are for illustrative purposes and are not intended to apply to any specific compound or product. Applicable information about a specific product or material shall be supplied in the appropriate block of the MSDS.

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the guidelines in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "100 ppm LC50 rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flammable or reactive data

could be flash point, shock sensitivity, or other brief data indicating nature of the hazard.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicate if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a time-weighted average (TWA) concentration, as a permissible exposure, or by some other indication of an acceptable limit. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, irritation, and cracking. Readily absorbed through the skin with severe systemic effects.

Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed workers.



(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect workers assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal anti-pollution ordinances" are proper but not sufficient. Specific procedures should be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If Necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Specify respirators as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to workers potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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## MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.	
ADDRESS		
TRADE NAME		
SYNONYMS		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H <sub>2</sub> O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H <sub>2</sub> O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

<b>IV FIRE AND EXPLOSION DATA</b>				
FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE		
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER	
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
<b>V HEALTH HAZARD INFORMATION</b>				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN:				
INHALATION:				
INGESTION				
NOTES TO PHYSICIAN				

<b>VI REACTIVITY DATA</b>
CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPOSITION PRODUCTS
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION
<b>VII SPILL OR LEAK PROCEDURES</b>
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED
NEUTRALIZING CHEMICALS
WASTE DISPOSAL METHOD
<b>VIII SPECIAL PROTECTION INFORMATION</b>
VENTILATION REQUIREMENTS
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT
RESPIRATORY (SPECIFY IN DETAIL)
EYE
GLOVES
OTHER CLOTHING AND EQUIPMENT

**IX SPECIAL PRECAUTIONS**

**PRECAUTIONARY  
STATEMENTS**

**OTHER HANDLING AND  
STORAGE REQUIREMENTS**

**PREPARED BY**

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**ADDRESS**

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**DATE**

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