IX. APPENDIX I

METHOD FOR SAMPLING 1,1,2,2-TETRACHLOROETHANE IN AIR

The sampling and analytical methods described here and in Appendix II are based on those described in Method No. S124 of NIOSH Analytical Methods [69].

General Requirements

(a) Collect air samples from within the breathing zones of workers to characterize the exposure from each job or specific operation in each work area.

(b) Collect samples representative of exposures of individual workers.

(c) Record the following:

(1) Date and time of sample collection.

(2) Sampling rate and duration and total sample volume.

(3) Location of sampling.

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

(5) Other pertinent information.

Sampling

(a) Collect samples in the breathing zones of workers without interfering with their freedom of movement.

(b) Collect samples to permit determination of TWA workday exposures for every job involving exposure to tetrachloroethane in sufficient numbers to express the variability of the exposures for the work situation.

(c) Apparatus for Charcoal-Tube Sampling

(1) Battery-operated sampling pump and a clip for attachment to workers' clothing: Airflow through the pump shall be within 5% of the desired rate.

(2) Charcoal tubes: Glass tubes with both ends flame-sealed, 7 cm long with a 6-mm outer diameter and a 4-mm inside diameter, and containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The adsorbing section contains 100 mg of charcoal; the backup section has 50 mg. A 3-mm portion of urethane foam is inserted between the outlet end of the tube and the backup section, and a plug of silylated 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 flow rate of 1 liter/minute.

(d) Calibration of Sampling Instruments

(1) Calibrate air sampling instruments with a representative charcoal tube in line over a normal range of flowrates (50-1,000 ml/minute). Establish calibration curves for each sampling pump and use them in adjusting the pump prior to and during each field use. Establish new calibration curves for each sampling pump any time repairs are made or when the sampling system is modified.

(2) Spot check the volumetric flow rate through the sampling system and make the proper adjustments before and during each study to ensure that accurate airflow data are obtained.

(e) Collection and Handling of Samples

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

(2) Position the smaller, backup section of the charcoal tube nearest the sampling pump. Tubing may be used to connect the back of the tube to the pump, but air being sampled should not pass through any hose or tubing before the charcoal tube.

(3) Place the charcoal tube in a vertical position with the inlet face down during sampling.

(4) To determine a TWA concentration, take two 4-hour samples, each at a flow rate of 100 ml/minute, to give a total volume of 24 liters/4-hour sample.

(5) Cap the charcoal tubes with inert plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

(6) Handle (break, seal, transport) one charcoal tube, which will be an analytical blank, in the same manner as the sample tubes but draw no air through it.

X. APPENDIX II

ANALYTICAL METHOD FOR 1,1,2,2-TETRACHLOROETHANE

Principle of the Method

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

(b) The tetrachloroethane 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 sampling and analytical method is intended to provide a measure of airborne tetrachloroethane in the range of 0.5-15 ppm. This method has been validated for a 10-liter sample only over the range of 2.3-10 ppm; however, it was stated in the validation report [69] that the method is useful over the extended range (0.5-15 ppm) necessary for the recommended standard.

(b) The lower limit of this method is determined by the efficiency with which small amounts of tetrachloroethane can be desorbed from the charcoal. Desorption efficiency must be determined over the range used.

(c) The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of tetrachloroethane and other substances in the air. When a test atmosphere containing 14.4 ppm of tetrachloroethane was sampled at 0.185 liter/minute for 4 hours, the first section of the charcoal tube held at least 4.5 mg of tetrachloroethane. During the sampling, the concentration of tetrachloroethane in the effluent was less than 5% of that in the influent, thus indicating that no breakthrough had occurred. If it is suspected that a particular atmosphere contains a large amount of contaminant, a smaller volume of sample should be collected.

Interferences

(a) Tetrachloroethane may not be trapped efficiently when the amount of water in the air is so great that condensation occurs in the charcoal sampling tube.

(b) When compounds other than tetrachloroethane are known or thought to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

(c) Any compound which has the same retention time as tetrachloroethane at the gas chromatographic conditions described in this method will interfere with the analysis. This type of interference may be eliminated by using a different column packing.

Precision and Accuracy

(a) The coefficient of variation for the total analytical and sampling method in the range of 16-70 mg/cu m (2.3-10 ppm) was 0.057 [69]. This value corresponds to a 2-mg/cu m (0.3-ppm) standard deviation at a level of 35 mg/cu m (5 ppm).

(b) On the average, the concentration values obtained at the 35-mg/cu m (5 ppm) level with the overall sampling and analytical method were 5.6% higher than the "true" concentrations for a limited number of laboratory experiments [69]. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentrations. Therefore, no recovery correction should be applied to the final result.

Advantages of the Method

(a) The analytical method provides one basic method for determining many different organic compounds.

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

(c) The analysis can be accomplished rapidly.

Disadvantages of the Method

(a) The amount of sample which can be taken is limited by the capacity of the charcoal tube before overloading. When the sample value obtained for the backup section of charcoal exceeds 25% of that for the front section, the possibility of appreciable sample loss exists.

(b) The precision of the method is limited by the reproducibility of the pressure drop across the tubes. Because the pump is usually calibrated for only one tube, variability in this drop will effect flow rate and will cause the sample volume to be in error.

Apparatus

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

(b) Stainless steel column (10 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 areas.

(d) Glass-stoppered microtubes of 2.5-ml capacity or 2-ml vials that can be sealed with inert caps.

(e) Microliter syringes: 10-μl and other convenient capacities for making standards and sample injections.

(f) Pipets: 1.0-ml delivery pipets.

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

Reagents

(a) "Spectroquality" carbon disulfide.

(b) Tetrachloroethane, preferably "spectroquality."

(c) Purified nitrogen.

(d) Prepurified hydrogen.

(e) Filtered compressed air.

Analysis of Samples

(a) Wash all equipment used for the analysis in detergent, followed by appropriate tap and distilled water rinses.

(b) Preparation of samples: With a file, score each charcoal tube in front of the first section of charcoal, and break it open. Remove and discard the glass wool. Transfer the charcoal in the first (larger) section to a small stoppered test tube. Remove and discard the separating foam. Transfer the second section of charcoal to another, similar test tube. Analyze these two sections separately.

(c) Desorption of samples: Prior to analysis, pipet 1.0 ml of carbon disulfide into each test tube to desorb tetrachloroethane from the charcoal. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

> BE EXTREMELY CAUTIOUS AT ALL TIMES WHEN USING CARBON DISULFIDE BECAUSE IT IS HIGHLY TOXIC, FLAMMABLE, AND EXPLOSIVE. IT CAN BE IGNITED BY HOT STEAM PIPES. PERFORM ALL WORK WITH CARBON DISULFIDE UNDER AN EXHAUST HOOD.

(d) Typical chromatographic operating conditions:

(1) 50 ml/minute (60 psig) nitrogen carrier gas flow.
(2) 65 ml/minute (24 psig) hydrogen gas flow to detector.
(3) 500 ml/minute (50 psig) airflow to detector.
(4) 175 C injector temperature.
(5) 230 C manifold temperature (detector).
(6) 160 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 and to increase accuracy and reproducibility of the sample volume injected, use the solvent-flush injection technique. First, flush the 10-μl syringe with carbon disulfide several times to wet the barrel and plunger. Draw 3 μl of carbon disulfide into the syringe. Remove the needle from the carbon disulfide solvent, and pull the plunger back about 0.2 μl to separate the solvent flush from the sample with an air pocket which will serve as a marker. Immerse the needle in the sample and withdraw a 5-μl aliquot, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After removing the needle and prior to injecting the sample, pull the plunger back a short distance to minimize evaporation of the sample from the tip of the needle. Make duplicate injections of each sample and standard. No more than a 3% difference in peak area is to be expected.

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

Determination of Desorption Efficiency

It is necessary to determine the percentage of tetrachloroethane that is removed from the charcoal in the desorption process. This desorption efficiency is determined at least once for a given compound for each batch of charcoal used.

Place 100 mg of charcoal, equivalent to the amount in the first section of a sampling tube, in a 2-inch-long tube with an inside diameter of 4 mm and flame-sealed at one end. This charcoal must be from the same batch as that used in collecting the samples and can be obtained from unused sampling tubes. Cap the open end with an inert plastic film. Inject a known amount of tetrachloroethane through the plastic cap directly into the charcoal with a microliter syringe, and recap the tube with inert plastic film. The amounts of tetrachloroethane injected should be in the expected concentration range of that found in the samples.

Prepare at least five tubes for each concentration in this manner and let them stand for at least 12 hours to ensure complete adsorption of tetrachloroethane onto the charcoal. These five tubes are the "desorption samples." Treat a parallel blank tube in the same manner except add no tetrachloroethane to it. Desorb and analyze the desorption samples and blanks in exactly the same manner as previously described.

Prepare two or three desorption standards for analysis by injecting the same volume of tetrachloroethane into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the desorption samples. Analyze these 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

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

The desorption efficiency is dependent on the amount of tetrachloroethane recovered from the charcoal. Plot the desorption efficiency versus weight of tetrachloroethane found. This curve is used in Calculations, subsection (e), to correct for adsorption losses when sample concentrations are calculated.

Calibration and Standards

It is convenient to express the concentrations of standards in terms of mg tetrachloroethane/1.0 ml of carbon disulfide because samples are desorbed in this amount of carbon disulfide. To minimize error, inject 10 times the desired weight of tetrachloroethane into 10 times the desired volume of carbon disulfide. For example, to prepare a 0.3 mg/1.0 ml standard, inject 3.0 mg (1.88 μl) of tetrachloroethane into a glass-stoppered flask containing exactly 10 ml of carbon disulfide. Use the density of tetrachloroethane (1.60 g/ml) to convert 3.0 mg into microliters that are easily measured with a microliter syringe. Prepare a series of standards varying in concentration over the appropriate range, and analyze under the same gas chromatographic conditions and at the same time as the unknown samples. To establish standard curves, plot concentration in mg/1.0 ml versus average peak area.

Calculations

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

(b) Subtract the weight of tetrachloroethane present in the front section of the blank charcoal tube from the weight of tetrachloroethane in the front section of the sample charcoal tube to give a corrected weight for the front section.

(c) Subtract the weight of tetrachloroethane present in the backup section of the blank charcoal tube from the weight of that in the backup section of the sample charcoal tube to give a corrected weight for the backup section.

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

(e) Read the desorption efficiency (DE) from the curve (see Determination of Desorption Efficiency) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

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

(f) The concentration of tetrachloroetane in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg} \times 1000 \text{ (liters/cu m)}}{\text{air volume sampled (liters)}}$$

(g) Concentration may also be expressed in ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{168} \times \frac{760}{P} \times \frac{t + 273}{298}$$

where:

P = pressure (mmHg) of air sampled

t = temperature (C) of air sampled

24.45 = molar volume (liter/mole) at 25 C and 760 mmHg

168 = formula weight (g/mole) of tetrachloroethane

760 = standard pressure (mmHg)

298 = average room temperature (K)

X. APPENDIX III

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (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 rules 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, eg, "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. Flashpoint, shock sensitivity or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(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 (indicated 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 flashpoint 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 TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. 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, possibly mild irritation.
>
> 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 employees.

(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 employees 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 antipollution ordinances" are proper but not sufficient. Specific procedures shall 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. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," 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 employees exposed to the hazardous substance. 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.

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_2O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

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					

V HEALTH HAZARD INFORMATION

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

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPOSITION PRODUCTS
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED NEUTRALIZING CHEMICALS
WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

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

ADDRESS:

DATE:

XII. APPENDIX IV

PHYSICAL AND CHEMICAL PROPERTIES OF 1,1,2,2-TETRACHLOROETHANE

Molecular formula	$CHCl_2 - CHCl_2$
Formula weight	167.9
Boiling point at 760 mmHg	146.3 C
Melting point	-36 C
Vapor pressure	5 mmHg at 21 C; 10 mmHg at 32 C
Specific gravity at 20 C (water = 1.000 at 4 C)	1.596
Solubility	0.29 g/100 g water at 25 C; miscible with most organic solvents
Explosive limit	None
Flashpoint	None
Vapor density (air = 1)	5.79
Conversion factors (760 mmHg and 25 C)	1 mg/l = 145.5 ppm 1 mg/cu m = 0.146 ppm 1 ppm = 6.87 μg/l 1 ppm = 6.87 mg/cu m

Adapted from 2-4

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DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

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