OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETYLENE TETRABROMIDE

INTRODUCTION

This guideline summarizes pertinent information about acetylene tetrabromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

• Formula

CHBr₂CHBr₂

Structure

• Synonyms

Tetrabromacetylene, tetrabromoethane; symmetrical tetrabromoethane; 1,1,2,2-tetrabromoethane (TBE); Muthmann's liquid

• Identifiers

1. CAS No.: 79-27-6

2. RTECS No.: KI8225000

3. DOT UN: 2504 58

4. DOT label: St. Andrew's Cross

Appearance and odor

Acetylene tetrabromide is a noncombustible, heavy, pale yellow liquid with a pungent, camphorlike odor. No quantitative data is available on the odor threshold.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 345.7

2. Boiling point (at 760 mm Hg): 239℃ (462.2°F)

3. Specific gravity (water = 1): 2.96 at 20°C (68°F)

 Vapor density (air - 1 at boiling point of acetylene tetrabromide): 11.9

5. Melting point: 0°C (32°F)

6. Vapor pressure at 20°C (68°F): 0.02 mm Hg

7. Solubility: Insoluble in water; miscible with alcohol, chloroform, ether, aniline, glacial acetic acid; soluble in acetone and benzene.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat

2. Incompatibilities: Toxic vapors may result from contact with chemically active metals or strong caustics, or with hot iron, aluminum, or zinc in the presence of steam.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, carbonyl bromide, brominated solvents, and carbon monoxide) may be released when acetylene tetrabromide decomposes.

4. Special precautions: Acetylene tetrabromide softens or destroys most plastics and rubbers.

Flammability

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to acetylene tetrabromide; this substance is not combustible.

1. Flash point: -18°C (0°F) (closed cup)

Autoignition temperature: 335°C (635°F)

3. Flammable limits in air: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES

Public Health Service Centers for Disease Control National Institute for Occupational Safety and Health Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use water to cool containers of acetylene tetrabromide that are involved in a fire.

Fires involving acetylene tetrabromide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetylene tetrabromide. Chemical protective clothing that is specifically recommended for acetylene tetrabromide may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetylene tetrabromide.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetylene tetrabromide is 1 ppm (14 mg/m³) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for acetylene tetrabromide [NIOSH 1988, 1991].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetylene tetrabromide a threshold limit value (TLV) of 1 ppm (15 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The OSHA and ACGIH limits are based on the risk of hepatotoxic effects associated with exposure to acetylene tetrabromide.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acetylene tetrabromide can occur through inhalation of the vapors, ingestion of the liquid, and eye or skin contact with the liquid or vapors.

Summary of toxicology

1. Effects on Animals: Acetylene tetrabromide is a central nervous system depressant and a liver, kidney, and lung toxin in animals. When instilled into the eyes of rabbits, the liquid

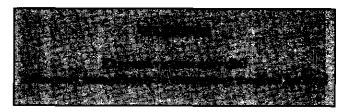
caused slight conjunctival and superficial comeal injury; on the skin of rabbits, a 24-hr application of 500 mg caused a moderate degree of irritation [NIOSH 1991]. The dermal LD₅₀ in rats is 5,250 mg/kg [NIOSH 1991]. The inhalation LC₅₀ in rats has been reported as 39 ppm (549 mg/m³) [NIOSH 1991]. Although no noteworthy effects were described for rats, rabbits, and guinea pigs exposed to saturated vapors (unquantified) for up to 2 hr, 3-hr exposures produced respiratory tract irritation, tremors, and CNS depression (ataxia, loss of the righting reflex, and unconsciousness). Only the guinea pigs died, each having postmortem fatty degeneration of the hepatic and renal parenchyma. The tissues for all survivors from the four species appeared histologically normal [Gray 1950]. Female rats exposed to saturated vapors (~14 ppm at 23°C) for 7 hr did not die and had very slight eye and nasal irritation [Hollingsworth et al. 1963]. The oral LD₅₀ in rats is 1,100 mg/kg [NIOSH 1991]. In a subchronic study, rats, rabbits, mice, and a monkey were exposed to ambient concentrations of 1, 4, or 14 ppm for 7 hr/day, 5 days/week for approximately 28, 26, or 15 weeks, respectively. The no observable effect level (NOEL) was 1 ppm. The 4-ppm concentration induced slight lung hemorrhage, congestion, edema, slight hepatocellular centrolobular fatty degeneration, and slight swelling of the renal convoluted tubules. Similar pulmonary and liver changes were reported at 14 ppm [Hollingsworth 1963]. Application of 15 mg to the skin of mice, followed 14 days later with a tumor-promoting agent (phorbol myristate acetate) caused a statistically significant increase in forestomach papillomas [Van Duuren et al. 1979; Proctor et al. 1988; NLM 1991].

2. Effects on Humans: Acetylene tetrabromide is a central nervous system depressant and a liver toxin in humans. When a chemist was exposed to this substance for 7.5 hr at an estimated concentration of 1 to 2 ppm with a single 10-min peak exposure to 16 ppm, he experienced headache, anorexia, nausea, vomiting, and abdominal pain. During a 9-week hospitalization, clinical studies revealed icterus, urobilinuria, bilirubinuria, and severe and nearly fatal liver damage [Proctor et al. 1988; Clayton and Clayton 1981]. Skin absorption of acetylene tetrabromide may also have been involved in this episode of acute poisoning [Proctor et al. 1988; ACGIH 1991a].

Signs and symptoms of exposure

1. Acute exposure: Acute exposure to acetylene tetrabromide can cause irritation of the eyes, nose, and upper respiratory tract; headache; nausea; vomiting; anorexia; abdominal pain; ataxia; CNS depression; and death. Jaundice, urobilinuria, bilirubinuria, and monocytosis have also been reported. Exposure to the eyes or skin with liquid acetylene tetrabromide may cause pain, redness, and a slight but reversible conjunctival irritation and corneal injury. 2. Chronic exposure: On the basis of effects seen in animals, exposure to acetylene tetrabromide can cause liver, kidney, and lung damage.

Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

- 1. Eye exposure: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetylene tetrabromide. Immediately and thoroughly flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Skin irritation may result. Immediately remove contaminated clothing and thoroughly wash contaminated skin with soap and water.
- 3. Inhalation exposure: If vapors, mists, or aerosols of acetylene tetrabromide are inhaled, move the victim to fresh air immediately. Have the victim blow his or her nose to remove residues from nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

- 4. Ingestion exposure: Take the following steps if acetylene tetrabromide or any material containing it is ingested:
- —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.
- -Have the victim drink a glass (8 oz) of fluid such as water.
- —Induce vomiting by giving syrup of ipecae as directed on the package. If ipecae is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.
- —Do not force an unconscious or convulsing person to drink fluid or to vomit.
- 5. Rescue: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acetylene tetrabromide may result in worker exposures to this substance:

- —Use as a catalyst or catalytic initiator in manufacture of terephthalic acid and synthetic fibers and as a polymer additive in flameproof, flame-retardant polystyrenes, polyurethanes, and polyolefins
- -Use in the density separation of mineral salts
- Use as a mercury substitute in gauges, as a level indicator in sight gauges, and as a refractive index liquid in microscopy
- -Use as a solvent for fats, oils, and waxes
- -Use as an ore flotation agent

The following methods are effective in controlling worker exposures to acetylene tetrabromide, depending on the feasibility of implementation:

- -Process enclosure
- —Local exhaust ventilation
- -General dilution ventilation
- -Personal protective equipment

Good sources of information about control methods are as follows:

- 1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- 2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- 3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
- 4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
- 5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to acetylene tetrabromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetylene tetrabromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with impaired liver function.

Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetylene tetrabromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetylene tetrabromide on the eyes, skin, upper respiratory tract, liver, and kidneys. Liver function studies should be performed on a routine basis, particularly in workers exposed to acetylene tetrabromide levels near the PEL. Current health status should be compared with the baseline health status of the

individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetylene tetrabromide.

Medical examinations recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetylene tetrabromide is determined by using a silica gel absorption tube (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. The sample is then treated with tetrahydrofuran to extract the acetylene tetrabromide. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.16. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 2003 of the NIOSH Manual of Analytical Methods [NIOSH 1984].

PERSONAL HYGIENE

If acetylene tetrabromide contacts the skin, workers should immediately wash the affected areas thoroughly with soap and water.

Clothing and shoes contaminated with acetylene tetrabromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of acetylene tetrabromide.

A worker who handles acetylene tetrabromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetylene tetrabromide is handled, processed, or stored.

STORAGE

Acetylene tetrabromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of acetylene tetrabromide should be protected from physical damage and should be stored separately from chemically active metals and strong caustics, heat, sparks, and open flame. Because empty containers may contain acetylene tetrabromide residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetylene tetrabromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

- 1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
- 2. Notify safety personnel.
- 3. If feasible, remove leaking containers to a safe place.
- 4. Ventilate atmosphere to reduce vapors.
- 5. Absorb small spills with sand, vermiculite, or other non-combustible absorbent material and place the material in a covered container for later disposal.
- 6. For large liquid spills, build dikes far ahead of the spill to contain the acetylene tetrabromide for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

Emergency planning requirements

Acetylene tetrabromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

Reportable quantity requirements for hazardous releases

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center about an accidental release of acetylene tetrabromide; there is no reportable quantity for this substance.

Community right-to-know requirements

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the annual amount of acetylene tetrabromide emitted or released from their facility.

• Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetylene tetrabromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetylene tetrabromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

Respiratory protection program

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel,

fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the NIOSH Respirator Decision Logic [NIOSH 1987b] and the NIOSH Guide to Industrial Respiratory Protection [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with acetylene tetrabromide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Such clothing may include gloves with long sleeves, aprons, footwear, and face shields. No reports have been published on the resistance of various protective clothing materials to permeation by acetylene tetrabromide; however, Viton®, Teflon®, and polyvinyl alcohol materials have been tested against permeation by a similar compound (ethylene dibromide) and have been found to provide good-to-excellent protection. These materials provided more than 8 hr of resistance to permeation by ethylene dibromide. Since specific test data are not available for acetylene tetrabromide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to acetylene tetrabromide.

If acetylene tetrabromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Chemical safety glasses, goggles, or face shields should be worn during operations in which acetylene tetrabromide might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetylene tetrabromide. Contact lenses should not be worn if the potential exists for acetylene tetrabromide exposure.

REFERENCES CITED

ACGIH [1991a]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1991b]. 1991-1992 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

Clayton G, Clayton F, eds. [1981]. Patty's industrial hygiene and toxicology. 3rd rev. ed. New York, NY: John Wiley & Sons.

Gray MG [1950]. Effects of exposure to the vapors of tetrabromoethane (acetylene tetrabromide). Arch Ind Hyg Occup Med 2:407-409.

Hollingsworth R, Rose V, Oyen F [1963]. Toxicity of acetylene tetrabromide determined on experimental animals. Ind Hyg J 24:28-35.

NIOSH [1984]. 1,1,2,2-Tetrabromoethane: Method 2003 (supplement issued 5/15/85). In: Eller PM, ed. NIOSH manual of analytical methods. 3rd rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. Respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1988]. Testimony of the National Institute for Occupational Safety and Health on the Occupational Safety and Health Administration's proposed rule, 29 CFR 1910, August 2, 1988, OSHA Docket No. H-020. NIOSH policy statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health.

NIOSH [1991]. Registry of toxic effects of chemical substances database: 1,1,2,2-tetrabromoethane. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

NLM [1991]. The hazardous substances data bank: 1,1,2,2-tetrabromoethane. Bethesda, MD: National Library of Medicine.

OSHA [1989]. Computerized information system.

Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

Proctor NH, Hughes JP, Fischman ML [1988]. Chemical hazards of the workplace. 2nd ed. Philadelphia, PA: J.B. Lippincott Company.

Van Duuren B, Goldschmidt B, Loewengart G, Smith A, Melchionne S, Seldman I, Roth D [1979]. Carcinogenicity of halogenated olefinic and alphatic hydrocarbons in mice. JNCI 63(2):1433-1439.

