OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMOFORM

INTRODUCTION

This guideline summarizes pertinent information about bromoform 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 Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CHBr_3$

- **Synonyms**

Tribromomethane, methenyl tribromide, methyl tribromide

- **Identifiers**

1. CAS No.: 75-25-2
2. RTECS No.: PB5600000
3. DOT UN: 2515 58
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Bromoform is a nonflammable, colorless-to-dark-brown, fuming, volatile liquid with a suffocating chloroformlike odor; it may form hexagonal crystals at 6° to 7°C (43° to 45°F). The odor threshold is reported to be 1.3 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 252.8
2. Boiling point (at 760 mm Hg): 149° to 150°C (300.2° to 302°F)
3. Specific gravity (water = 1): 2.9 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of bromoform): 8.7
5. Melting point: 8.3°C (46.9°F)
6. Vapor pressure at 20°C (68°F): 5 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, benzene, chloroform, ether, petroleum ether, acetone, and oils
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires and explosions may result from contact of bromoform with chemically active metals (sodium, potassium, powdered aluminum, zinc, magnesium, lithium), calcium, acetone, or strong caustics (such as potassium hydroxide).
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide, bromine, hydrogen bromide, and bromine oxides) may be released in a fire involving bromoform.
4. Special precautions: Liquid bromoform attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to bromoform; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air (% by volume): Not applicable

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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: Bromoform itself does not burn; use an extinguishant that is suitable for the material involved in the surrounding fire.

Fires involving bromoform 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. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromoform. Chemical protective clothing that is specifically recommended for bromoform may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromoform.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromoform is 0.5 ppm (5 mg/m^3) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 ppm (5 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromoform a threshold limit value (TLV) of 0.5 ppm (5.2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a "Skin" notation [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of irritation and liver damage associated with exposure to bromoform.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to bromoform can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• **Summary of toxicology**

1. *Effects on Animals*: Bromoform is an irritant of the eyes, skin, and respiratory tract; a central nervous system depressant; and a liver and kidney toxin. The application of undiluted bromoform to the eyes of rabbits caused moderate irritation that healed within 1 or 2 days. Rabbits also acutely exposed dermally to undiluted bromoform (2,000 mg/kg) developed moderate skin irritation but did not die [Clayton and Clayton 1981]. Rabbits exposed to 1,070 to 1,270 ppm for an unspecified duration developed narcosis [Clayton and Clayton 1981]. A dog exposed for 1 hr to approximately 7,000 ppm experienced deep narcosis followed by death [ACGIH 1991a]. The oral LD_{50}s for male and female rats were 1,388 and 1,147 mg/kg, respectively. Exposure of rabbits to 243 ppm for 10 days resulted in functional changes in the central nervous system, liver, and kidneys plus vascular and dystrophic changes [Clayton and Clayton 1981]. Rats exposed to 24 ppm for 4 hr/day for 2 months developed disorders in liver prothrombin synthesis and glycogenesis as well as reduced renal filtration capacity [NLM 1991]. Bromoform was mutagenic when tested in three strains of *Salmonella typhimurium* [ACGIH 1991a]. Carcinogenicity bioassays were performed with mice and rats treated by gavage with various doses of bromoform for 5 days/week during 103 weeks. Although the male and female rats in these bioassays showed an increased incidence of adenomatous polyps or adenocarcinomas of the large intestine, the mice were unaffected by treatment [NTP 1989]. Mice given repeated intraperitoneal injections of bromoform developed a significantly increased incidence of pulmonary adenomas [Theiss et al. 1977].

2. *Effects on Humans*: Bromoform has both narcotic and irritant effects in humans. Exposure to the vapor at unspecified concentrations causes irritation of the eyes, respiratory tract, pharnyx, and larnyx [Proctor et al. 1988]. Prolonged contact with the skin may lead to skin burns [NLM 1991]. Accidental ingestion of bromoform has produced central nervous system depression with coma and loss of reflexes; small doses have led to listlessness, headache, and vertigo [ACGIH 1991a].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to bromoform can cause irritation, tearing, headache, dizziness, vertigo, digestive symptoms, weight loss, excessive salivation, lethargy, sedation, amnesia, shock, convulsions, anesthesia, pulmonary edema, respiratory failure, and death.

2. *Chronic exposure*: No signs or symptoms of chronic bromoform exposure have been reported.

- **Emergency procedures**

[illegible]

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 bromoform. ***Immediately and thoroughly*** flush 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 bromoform are inhaled, move the victim to fresh air ***immediately***.

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 bromoform or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

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 bromoform may result in worker exposures to this substance:

—Use as a reagent for graphite ore fractionation and as a heavy liquid flotation agent in mineral separation for sedimentary petrographical surveys, geological assays, and purification of materials such as quartz

—Use in the shipbuilding, aircraft, and aerospace industries

—Use as a solvent for waxes, greases, oils, and fats

—Use as an ingredient in fire-resistant chemicals and gauge fluids

—Use as an ingredient in pharmaceuticals and medicinal products such as antiseptics, sedatives, and cough suppressants

The following methods are effective in controlling worker exposures to bromoform, 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 bromoform, 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 central nervous system, liver, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

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 bromoform at or below the prescribed exposure limit. The 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 central nervous system, liver, kidney, or respiratory system diseases.

- **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 bromoform exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromoform on the central nervous system, liver, kidneys, and respiratory tract. 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 tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Inorganic bromide can be detected in the serum of bromine-exposed workers. Some sources suggest that the serum bromide concentration in bromoform-exposed workers should not exceed 15 to 30 mg/liter of serum. However, because few data correlate airborne exposure concentrations with serum bromide concentrations, no biological monitoring test acceptable for routine use has yet been developed for bromoform.

- **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 bromoform is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 5 µg per sample. This method is described in Method 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If bromoform contacts the skin, workers should flush the affected areas immediately with plenty of water and then wash thoroughly with soap and water.

Clothing contaminated with bromoform should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of bromoform, particularly its potential for causing eye and respiratory tract irritation.

A worker who handles bromoform 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 bromoform or solutions containing bromoform are handled, processed, or stored.

STORAGE

Bromoform 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 bromoform should be protected from physical damage and should be stored separately from caustic alkalies, chemically active metals (such as sodium, potassium, powdered aluminum, zinc, magnesium, and lithium), calcium, acetone, heat, sparks, and open flame. Because containers that formerly contained bromoform may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromoform, 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. Ventilate the area of the spill or leak.

4. Absorb small spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

5. For large spills, build dikes far ahead of the spill to contain the bromoform for later reclamation or 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**

Bromoform 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**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for bromoform is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of bromoform per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromoform emitted or released from their facility annually.

- **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. Bromoform is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and it has been assigned EPA Hazardous Waste No. U225. Bromoform is approved for land disposal as long as the concentration of bromoform in the waste or treatment residual does not exceed 15 mg/kg. Bromoform also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

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 limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromoform 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 any possibility of skin contact with bromoform. 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. The following materials have been tested against permeation by bromoform and have demonstrated protection for periods greater than 8 hr: polyvinyl alcohol and Viton®. Butyl rubber has demonstrated questionable resistance to permeation by bromoform. Natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by bromoform.

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

Safety glasses, goggles, or face shields should be worn during operations in which bromoform 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 bromoform. Contact lenses should not be worn if the potential exists for bromoform exposure.

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