

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMINE

INTRODUCTION

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 Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information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



• Synonyms

Caswell No. 112

• Identifiers

1. CAS No.: 7726-95-6
2. RTECS No.: EF9100000
3. DOT UN: 1744 59
4. DOT label: Corrosive

• Appearance and odor

Bromine is a heavy, noncombustible, red-brown fuming liquid with an irritating and suffocating odor. The odor threshold is reported to be 0.05 to 3.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Atomic number: 35
2. Molecular weight: 159.8
3. Boiling point (at 760 mm Hg): 58.8°C (137.8°F)

4. Specific gravity (water = 1): 3.1 at 20°C (68°F)
5. Vapor density (air = 1 at boiling point of bromine): 3.5
6. Melting point: -7.2°C (18.9°F)
7. Vapor pressure: 172 mm Hg at 20°C (68°F); 100 mm Hg at 9.3°C (48.7°F)
8. Solubility: Very slightly soluble in water; freely soluble in alcohol, ether, carbon tetrachloride, carbon disulfide, aqueous solutions of bromides, chloroform, and concentrated hydrochloric acid.
9. Evaporation rate: Data not available

• Reactivity

1. Conditions contributing to instability: Bromine emits toxic fumes when it is heated or in contact with steam or water.
2. Incompatibilities: Bromine is a powerful oxidizer; in contact with organic or other readily oxidizable materials, it may cause fires and explosions. Contact of liquid bromine with aqueous ammonia or with metals may cause violent reactions. Anhydrous bromine reacts violently with aluminum, titanium, mercury, or potassium. Bromine is also incompatible with alkali hydroxides, arsenites, carbonyls, alcohols, ferrous and mercurous salts, hypophosphites, and many other substances.
3. Hazardous decomposition products: Toxic fumes may be released in a fire involving bromine.
4. Special precautions: Bromine attacks some coatings and some forms of plastic and rubber. This substance corrodes iron, steel, stainless steel, and copper.

• Flammability

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to bromine; however, it is a strong oxidizer and accelerates the burning of combustibles. The heat of such reactions may cause nearby combustible materials to ignite.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: 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: Use dry chemical, carbon dioxide, Halon[®], water spray, or alcohol foam to fight fires involving bromine. Because bromine can react with steam or with small amounts of water, containers should be cooled and surrounding fires should be extinguished by flooding with large amounts of water. Anhydrous ammonia vapor released from a safe distance can be used to neutralize large quantities of bromine vapor; do *not* use aqueous ammonia because it may react violently with liquid bromine.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromine. Chemical protective clothing that is specifically recommended for bromine may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromine is 0.1 ppm (0.7 mg/m³) as an 8-hr time-weighted average (TWA) concentration and 0.3 ppm (2 mg/m³) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [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 0.1 ppm (0.7 mg/m³) as an 8-hr TWA and 0.3 ppm (2 mg/m³) as a STEL [NIOSH 1992].

• ACGIH TLV[®]

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromine a threshold limit value (TLV) of 0.1 ppm (0.7 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (2 mg/m³) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of severe irritation of the eyes, mucous membranes, lungs, and skin associated with exposure to bromine.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Summary of toxicology

1. *Effects on Animals:* Bromine is a corrosive and severe irritant to the eyes, skin, mucous membranes, and respiratory tract in animals and can be rapidly fatal when inhaled. The lowest observed lethal concentration (LC_{Lo}) is 140 ppm for 7 hr in cats and guinea pigs and 180 ppm for 6.5 hr in rabbits [NIOSH 1991]. Cats, rabbits, and guinea pigs exposed to 180 ppm for 7 hr developed severe eye irritation with clouding of the cornea, severe irritation of the respiratory tract, and difficult breathing; at 23 ppm, however, the irritation and dyspnea was mild [NLM 1992]. Guinea pigs and rabbits exposed to 300 ppm for 3 hr developed lung edema, pseudo-membranous deposits on the trachea and bronchi, and hemorrhages of stomach mucosa. Animals that died several days after this exposure showed evidence of bronchopneumonia and central nervous system disturbances at autopsy [Clayton and Clayton 1981]. The 2-hr and 9-min LC_{50s} for mice are 240 and 750 ppm, respectively [ACGIH 1991a; NLM 1992]. Rats, mice, and rabbits inhaling 0.2 ppm of bromine for 4 months showed disturbances in respiratory, endocrine, and nervous system functioning; exposure to 0.02 ppm for the same interval caused no adverse effects [NLM 1992]. Rats fed 0.01 mg/kg bromine for 6 months showed changes in conditional reflexes and in several blood indices.

2. *Effects on Humans:* Bromine is corrosive to the eyes, skin, mucous membranes, and respiratory tract in humans. Eye contact can result in severe, painful, and destructive burns of the eyes [Sittig 1985; AIHA 1978]. Brief contact of the skin with liquid bromine causes vesicles and pustules, and prolonged contact leads to deep, painful burns that ulcerate and are slow to heal [Sittig 1985; Clayton and Clayton 1981]. Repeated contact of the skin with bromine in liquid or vapor form may cause dermatitis and halogen-acne [Rom 1983; Deichmann and Gerarde 1969]. Inhalation of airborne concentrations below 1 ppm causes tearing of the eyes; exposure to 4 ppm can be tolerated for only 30 to 60 min; 10 ppm induces respiratory damage and is considered immediately dangerous to life or health; and 30 ppm would cause death in a short time [Clayton and Clayton 1981; NIOSH 1987b; NLM 1992]. Acute nonlethal exposures can also induce coughing, nosebleed, feelings of oppression, dizziness, headache, and delayed onset of abdominal pain and measles-like dermal eruptions [NLM 1992]. Pulmonary edema may occur after several hours, and high concentrations can cause death from corrosive burns of the lung [Parmeggiani 1983; Sittig 1985]. The inhalation LC_{Lo} in humans is 1,000 ppm [NIOSH 1991]. The lowest lethal oral dose is estimated to be 14 mg/kg [NIOSH 1991]. Ingestion of the liquid produces corrosive tissue burns, mouth and esophageal pain, vomiting, diarrhea, shock (hypotension, tachycardia, cyanosis), headache, dizziness, delirium, collapse, and stupor. Death can result from glottic or pulmonary

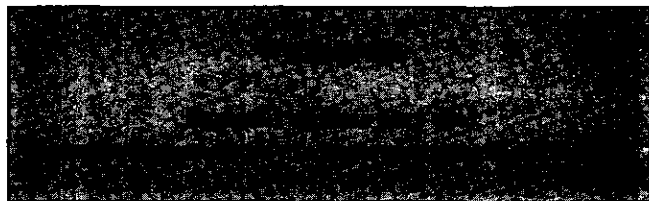
edema or aspiration pneumonia. Survivors can develop esophageal and pyloric stenoses [NLM 1992]. Regular exposure to 0.3 to 0.6 ppm for 1 year has induced headache, heart-area chest pain, irritability, anorexia, joint pain, and dyspepsia. Continued exposure for 5 to 6 years can cause loss of corneal reflexes, pharyngitis, vegetative disorders, thyroid hyperplasia and dysfunction, cardiovascular disorders (myocardial degeneration and hypotension), digestive tract secretory disorders, and inhibition of leucopoiesis and leucocytosis [NLM 1992].

• Signs and symptoms of exposure

1. *Acute exposure:* Acute exposure to bromine can cause irritation or corrosion of contacted tissues, tearing, corneal clouding, dizziness, headache, pulmonary edema, dyspnea, nosebleeds, coughing, bronchopneumonia, central nervous system disturbances, abdominal pain, diarrhea, altered conditioned reflexes, delirium, collapse, and death. Survivors of ingestion incidents can develop esophageal and pyloric stenoses.

2. *Chronic exposure:* Chronic exposure to bromine can cause contact irritation, slow healing, painful acne-like skin eruptions, headache, heart pain, irritability, anorexia, joint pain, dyspepsia, loss of corneal reflexes, pharyngitis, vegetative disorders, thyroid dysfunction, and cardiovascular and digestive disorders.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. *Immediately* initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of bromine! *Immediately but gently* flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! *Immediately* remove contaminated clothing! *Immediately and gently* wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* If vapors, mists, or aerosols of bromine are inhaled, move the victim to fresh air *immediately*.

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

4. *Ingestion exposure:* Take the following steps if bromine 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. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and *no more*.

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

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 operations may involve bromine and may result in worker exposures to this substance:

—Manufacture of ethylene dibromide, an anti-knock gasoline additive

—Use of bromine as a solvent

—Manufacture of pesticides

—Use of bromine in flame retardants for the plastics, fabric, and fiber industries

—Use of bromine as a sanitizing, disinfecting, bleaching, and water-purifying agent

—Manufacture of organic and inorganic compounds for use in photographic films and papers, sedatives, inks, anesthetics, hydraulic fluids, pharmaceuticals, fungicides, laboratory reagents, dyes and dyestuffs, war gases,

refrigerating and dehumidifying agents, and hair-waving preparations

—Use of bromine as a bleaching agent for silks and other fabrics, as a shrink-proofing agent for wool, as a desizing agent for cotton, and in gold extraction

The following methods are effective in controlling worker exposures to bromine, 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 bromine, 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 skin 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 bromine 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 skin 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 bromine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromine on the skin and respiratory system. 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. No biological monitoring test acceptable for routine use has yet been developed for bromine.

• 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 bromine is determined by using a midget fritted-glass bubbler containing 10 ml of a standard eluent carbonate-bicarbonate solution (0.003 M NaHCO_3 to 0.0024 M Na_2CO_3). Samples are collected at a maximum flow rate of 0.5 liter/min until a recommended air volume of 30 liters is collected. (Sampling may continue up to a maximum volume of 120 liters.) Analysis is conducted by ion chromatography. The limit of detection for this procedure is $6.7 \mu\text{g}/\text{m}^3$ for a 30-liter sample. This method is described in Method ID-108 of the *OSHA Analytical Methods Manual* [OSHA 1985]. An alternate method uses a silver membrane filter for sample collection, and ion chromatography for analysis with a limit of detection of $1.6 \mu\text{g}$ of bromine per sample. This method is described in Method 6011 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If bromine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then soak the affected areas in a 10% aqueous thiosulfate solution. Get medical help immediately.

Clothing and shoes contaminated with bromine 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 bromine, particularly its potential for being corrosive to the eyes, skin, and respiratory tract.

A worker who handles bromine 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 bromine or a solution containing bromine is handled, processed, or stored.

STORAGE

Bromine 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 bromine should be protected

from physical damage and should be stored separately from combustibles, organic or other readily oxidizable materials, ammonia, aluminum, titanium, mercury, potassium, alkali hydroxides, arsenites, ferrous and mercurous salts, hypophosphites, heat, sparks, direct sunlight, and open flame. Bromine should be stored at temperatures above -6.7°C (19.9°F) to prevent freezing; heating containers of bromine above atmospheric temperatures may rupture the containers. Because containers that formerly contained bromine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

Before bromine is handled in the workplace, an emergency plan for dealing with emergency spills or leaks of this substance must be developed. In the event of a spill or leak involving bromine, 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. Stay upwind of the spill or leak area to the extent possible.
4. Neutralize small liquid spills by pouring a hypo solution (sodium thiosulfate or limewater) over them; the spilled material can then be absorbed with sand or other noncombustible absorbent material and placed in a covered container for later disposal.
5. Neutralize large liquid spills with a solution of potassium carbonate, sodium carbonate, or sodium bicarbonate; or build a dike far ahead of the spill to contain the bromine for later reclamation or disposal.
6. Neutralize bromine vapors in air by carefully releasing anhydrous ammonia gas (do *not* use aqueous ammonia gas).

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**

If 500 lb or more of bromine is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **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 above 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, State, and local authorities.

The reportable quantity for bromine is 1 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 are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromine 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. Although bromine 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 limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromine 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 1987c] 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 bromine. Rubber boots, gloves, aprons, and full-body covering are recommended. 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. Teflon[®] has been tested against permeation by bromine and may provide good-to-excellent resistance for more than 4 but fewer than 8 hr. Polyethylene and natural rubber have been tested against bromine and have demonstrated poor resistance to permeation by bromine.

If bromine 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 bromine might contact the eyes (e.g., through contact with the vapor or 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 bromine. Contact lenses should not be worn if the potential exists for bromine exposure.

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