

Occupational Health Guideline for Methyl Bromide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH₃Br
- Synonyms: Bromomethane
- Appearance and odor: Colorless liquid or gas with a chloroform-like odor at high concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl bromide is a ceiling of 20 parts of methyl bromide per million parts of air (ppm). This may also be expressed as 80 milligrams of methyl bromide per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl bromide from 15 ppm to 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

• Routes of exposure

Methyl bromide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

• Effects of overexposure

1. Short-term Exposure: Methyl bromide may cause headache, dizziness, nausea, vomiting, blurred vision, slurred speech, and convulsions. High concentrations may cause unconsciousness and death. High concentrations may also cause lung irritation resulting in congestion with coughing, chest pain, and shortness of breath. Lung effects may be delayed in onset. Exposure may also result in kidney damage. The liquid splashed on

clothing, gloves, or shoes may be held in close contact with the skin and result in skin burns. Blisters commonly appear after several hours. If the exposure is less severe, an itching skin rash may appear after several days. Contact of liquid methyl bromide with the eyes may cause serious injury.

2. Long-term Exposure: Prolonged or repeated exposure to methyl bromide may cause a variety of symptoms and signs mostly due to injury of the central nervous system. These include visual disturbances, slurred speech, numbness of the arms and legs, confusion, shaking, and unconsciousness. The symptoms may stop within a few days after the termination of exposure or may last for several months. Usually recovery is complete.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl bromide.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to methyl bromide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. A careful history and examination of the nervous and respiratory systems should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Methyl bromide may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methyl bromide is reported to cause pulmonary impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

• **Summary of toxicology**

Methyl bromide gas is a severe pulmonary irritant and neurotoxin. It is also a narcotic at high concentrations. Rats did not survive when exposed to 12,850 ppm for 6 minutes, but did survive following exposure to 260 ppm for 8 hours; the no-effect level on repeated exposure was 16 ppm for all species. There are numerous reports of human intoxication from accidental exposure associated with its use in fire extinguishers and as a fumigant. Estimates of concentrations which have caused human fatalities range from 8000 ppm for a few hours to 60,000 ppm for a brief exposure. The onset of toxic symptoms is usually delayed, and the latent period may be from 30 minutes to several days. Early symptoms include headache, visual disturbances, nausea, vomiting, and malaise. In some cases eye irritation, vertigo, and tremors of the hands have occurred; the tremors may progress to twitchings and finally to convulsions. The onset of dyspnea may herald the development of pulmonary edema. Tubular damage in the kidneys has been observed in fatal cases. Some who recovered from severe intoxication have had persistent central nervous system effects including vertigo, depression, hallucinations, anxiety, and inability to concentrate. The determination of bromide in human blood has been proposed for the purpose of estimating the severity of exposure; in a few cases, levels of 40 mg/100 ml of blood have been associated with gross disability, while levels of 10 mg/100 ml and less have been followed by complete recovery. The procedure has not been sufficiently verified to recommend it for routine monitoring of occupational exposure. Local contact with the eye by the gas or liquid results in transient irritation and conjunctivitis. Repeated splashes of the liquid on the skin cause marked irritation with vesiculation; less severe exposures result in a dry, scaling, itching dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 94.9
2. Boiling point (760 mm Hg): 3.6 C (38.4 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of methyl bromide): 3.3
5. Melting point: -94 C (-137 F)
6. Vapor pressure at 20 C (68 F): 1.83 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): Greater than 1

• **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with aluminum or strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide and carbon

monoxide) may be released in a fire involving methyl bromide.

4. Special precautions: Liquid methyl bromide will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: None in standard test method
2. Autoignition temperature: 537 C (999 F)
3. Flammable limits in air, % by volume: (Only in presence of high energy ignition source) Lower: 13.5; Upper: 14.5
4. Extinguishant: Stop flow of gas.

• **Warning properties**

1. Odor Threshold: Both Patty and the AIHA *Hygienic Guide* report that methyl bromide has practically no odor. Grant notes, however, that at extremely high concentrations, methyl bromide has a "sweetish, not unpleasant odor."

2. Eye Irritation Level: Grant reports that methyl bromide "causes no immediate irritation of the eyes, . . . even at severely poisonous concentrations." Following a period of several hours after exposure to the gas, however, the victim may "have lacrimation from irritation of the eyes." Grant states that "local contact of methyl bromide with the eye, either as concentrated vapor or as a splash of liquid, has resulted in no more than transient irritation and conjunctivitis in the few cases in which this accident has been observed." He also reports that exposing a rabbit's eye to pure methyl bromide gas for 1-1/2 minutes resulted in an "immediate loss of surface luster, followed in several hours by a loss of corneal epithelium and much edema of the conjunctivae and lids." The cornea became opaque but began clearing within 5 days. Grant notes that this exposure was far more severe than that which would happen by accident.

3. Other Information: Grant reports that methyl bromide causes no immediate irritation of the "nose or respiratory tract, even at severely poisonous concentrations."

4. Evaluation of Warning Properties: Since methyl bromide has virtually no odor and no immediately irritating effects, it has poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methyl bromide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl bromide may be used. An analytical method for methyl bromide is in the *NIOSH* obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set J" (order number PB 263 959).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid methyl bromide.

• Clothing contaminated with liquid methyl bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl bromide, the person performing the operation should be informed of methyl bromide's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid methyl bromide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with liquid methyl bromide should be removed immediately and not reworn until the methyl bromide is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl bromide may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methyl bromide should be immediately washed or showered with soap or mild detergent and water to remove any methyl bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a space and soil fumigant in agriculture and industry	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in food sterilization for pest control in fruits, vegetables, dairy products, nuts, and grains	General dilution ventilation; local exhaust ventilation
Use in organic synthesis as methylating agent, for preparation of quaternary ammonium compounds and organo-tin derivatives; use as selective solvent in aniline dyes; laboratory procedures	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If methyl bromide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If methyl bromide gets on the skin, immediately flush the contaminated skin with water. If methyl bromide soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of methyl bromide, move the exposed person to fresh air at once. If

breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl bromide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If methyl bromide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

- **Waste disposal method:**

Methyl bromide may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methyl Bromide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Methyl Bromide," *Hygienic Guide Series*, Detroit, Michigan, 1958.
- Butler, E. C. B., et al.: "Methyl Bromide Burns," *British Journal of Industrial Medicine*, 2:30-31, 1945.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Hine, C. H.: "Methyl Bromide Poisoning," *Journal of Occupational Medicine*, 11:1-10, 1969.
- Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-35, Methyl Bromide*, Washington, D.C., 1968.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Rathus, E. M., and Landy, P. J.: "Methyl Bromide Poisoning," *British Journal of Industrial Medicine*, 18:53-57, 1961.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.
- von Oettingen, W. F.: *The Halogenated Aliphatic, Olefinic, Cyclic, Aromatic, and Aliphatic-Aromatic Hydrocarbons Including the Halogenated Insecticides, Their Toxicity and Potential Dangers*, U.S. Public Health Service Publication No. 414, U.S. Government Printing Office, Washington, D.C., 1955, pp. 15-30.
- Watrous, R. M.: "Methyl Bromide," *Industrial Medicine*, 11:12, pp.575-79, 1942.

RESPIRATORY PROTECTION FOR METHYL BROMIDE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Gas Concentration	
200 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

