

Occupational Health Guideline for Perchloromethyl Mercaptan

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: CCl_3SCl
- Synonyms: PMM; trichloromethylsulfur chloride; trichloromethanethiol; perchloromethanethiol
- Appearance and odor: Pale yellow, oily liquid with a foul-smelling, strong acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for perchloromethyl mercaptan is 0.1 part of perchloromethyl mercaptan per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.8 milligram of perchloromethyl mercaptan per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Perchloromethyl mercaptan 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 enter the body through the skin.

• Effects of overexposure

Inhalation of perchloromethyl mercaptan vapor may cause irritation of the eyes, nose, throat, and lungs as well as nausea. An exposure to this chemical by inhalation and skin contact has caused severe breathing difficulty and death. Liver and kidney damage also occurred following this exposure. The liquid splashed on the skin or in the eyes will cause irritation.

• 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 perchloromethyl mercaptan.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to perchloromethyl mercaptan 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. Examination of the eyes, respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to perchloromethyl mercaptan, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—14" x 17" chest roentgenogram: Perchloromethyl mercaptan causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Perchloromethyl mercaptan is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Perchloromethyl mercaptan has been reported to cause liver damage in humans. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

• Summary of toxicology

Perchloromethyl mercaptan vapor is a severe respiratory irritant and lacrimator. Mice and cats exposed for 15 minutes at 45 ppm died within 1 to 2 days from

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

pulmonary edema; 3-hour exposures at 9 ppm killed 50% of mice; repeated exposures over 3 months at 1 ppm resulted in the death of some mice. Eye irritation begins at 10 mg/m³ (1.3 ppm). Exposure at higher concentrations causes marked irritation of the eyes, throat, and bronchi, as well as nausea. Three chemical workers were observed following accidental exposures to perchloromethyl mercaptan; two survived episodes of pulmonary edema, while the third died after 36 hours. The fatality resulted from a spill of the liquid on clothing and floor with exposure to the vapor. At autopsy, there was necrotizing tracheitis, massive hemorrhagic pulmonary edema, marked toxic nephrosis, and vacuolization of centrilobular hepatic cells. The liquid splashed on the skin may be expected to cause irritation.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 185.9
2. Boiling point (760 mm Hg): 149 C (300 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of perchloromethyl mercaptan): 6.4
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 65 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble, reacts slowly to form hydrochloric acid, carbon dioxide, and sulfur.
8. Evaporation rate (butyl acetate = 1): Data not available

• Reactivity

1. Conditions contributing to instability: Perchloromethyl mercaptan decomposes at elevated temperatures to give carbon tetrachloride and sulfur monochloride. The decomposition is rapid at 149 C (300 F), the boiling point.

2. Incompatibilities: Contact with alkalis and amines may cause rapid decomposition. Contact with hot iron causes formation of toxic carbon tetrachloride vapor. Contact with hot water causes formation of hydrochloric acid, sulfur, and carbon dioxide.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon tetrachloride, sulfur monochloride, hydrogen chloride, sulfur dioxide, and carbon monoxide) may be released in a fire involving perchloromethyl mercaptan.

4. Special precautions: Perchloromethyl mercaptan will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible

• Warning properties

1. Odor Threshold: By analogy with other mercaptans, perchloromethyl mercaptan is assumed to have an odor threshold below the permissible exposure limit. In addition, the following odor thresholds for differ-

ent mercaptans can be found in May: n-butyl mercaptan, 0.00082 ppm; i-butyl mercaptan, 0.00054 ppm; i-pentyl mercaptan, 0.00021 ppm; i-amyl mercaptan, 0.00043 ppm; allyl mercaptan, 0.00005 ppm; crotyl mercaptan, 0.00016 and 0.000056 ppm; benzyl mercaptan, 0.0026 and 0.00035 ppm.

2. Eye Irritation Level: Grant states that perchloromethyl mercaptan "is a stink and tear gas that has been of military interest." No quantitative information is available, however, concerning the levels which produce eye discomfort.

3. Other Information: Grant states that this substance is a respiratory tract irritant.

4. Evaluation of Warning Properties: Since the odor threshold of perchloromethyl mercaptan is considerably below the permissible exposure limit and odor may be present within a properly functioning respirator, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

At the time of publication of this guideline, no measurement method for perchloromethyl mercaptan had been published by NIOSH.

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 repeated or prolonged skin contact with liquid perchloromethyl mercaptan.
- Clothing wet with perchloromethyl mercaptan should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of perchloromethyl mercaptan from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the perchloromethyl mercaptan, the person performing the operation should be informed of perchloromethyl mercaptan's hazardous properties.
- Non-impervious clothing which becomes wet with liquid perchloromethyl mercaptan should be removed promptly and not reworn until the perchloromethyl mercaptan is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid perchloromethyl mercaptan may contact the eyes.

SANITATION

- Skin that becomes wet with liquid perchloromethyl mercaptan should be promptly washed or showered with soap or mild detergent and water to remove any perchloromethyl mercaptan.
- Employees who handle liquid perchloromethyl mercaptan should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in chemical synthesis for agricultural and dye chemicals; use as an organic intermediate	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

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 liquid perchloromethyl mercaptan or strong concentrations of perchloromethyl mercaptan vapors get 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 liquid perchloromethyl mercaptan gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid perchloromethyl mercaptan soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of perchloromethyl mercaptan, 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 liquid perchloromethyl mercaptan has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **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 perchloromethyl mercaptan is spilled or leaked, the following steps should be taken:
 1. Ventilate area of spill or leak.
 2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.
- **Waste disposal methods:**
Perchloromethyl mercaptan may be disposed of:
 1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
 2. By dissolving in a combustible solvent, such as alcohol, and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- Althoff, H.: "Todliche Perchlormethylmercaptan - Intoxikation," *Archiv fur Toxikologie*, 31:121-135, 1973.
- American Conference of Governmental Industrial Hygienists: "Perchloromethyl Mercaptan," *Documentation of the Threshold Limit Values for Substances in*

Workroom Air (3rd ed., 2nd printing), Cincinnati, 1974.

• Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

• May, J.: "Solvent Odor Thresholds for the Evaluation of Solvent Odors in the Atmosphere," *Staub-Reinhalt*, 26:9, 385-389, 1966.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR PERCHLOROMETHYL MERCAPTAN

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Vapor Concentration	
1ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 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.