OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR METHYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about methyl mercaptan for workers, employers, and 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 Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** CH_4S
- **Structure:** CH_3—SH
- **Synonyms:** Mercaptomethane, methanethiol, methyl sulfhydrate, thiomethyl alcohol
- **Identifiers:** CAS 74-93-1; RTECS PB4375000; DOT 1064, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with an odor like decaying cabbage

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 48.11
2. Boiling point (at 760 mmHg): 5.96°C (40.4°F)
3. Specific gravity (water = 1): 0.8665
4. Vapor density (air = 1 at boiling point of methyl mercaptan): 1.66
5. Melting point: -123°C (-190°F)
6. Vapor pressure at 20°C (68°F): 1,276 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 2.4
8. Ionization potential: 9.44 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents. Elevated temperature may generate high internal pressure and cause containers to burst.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving methyl mercaptan.
3. Caution: Liquid methyl mercaptan will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -18°C (0°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 3.9; upper, 21.8
3. Extinguishant: Carbon dioxide, dry chemicals, or alcohol foam
4. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 1 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, methyl mercaptan can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for methyl mercaptan is 10 parts of methyl mercaptan per million parts of air (ppm) [20 milligrams of methyl mercaptan per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.5 ppm (1.0 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1 mg/m^3) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for methyl mercaptan

	Exposure limits	
	ppm	mg/m^3
OSHA PEL ceiling	10	20
NIOSH REL ceiling (15 min)	0.5	1.0
ACGIH TLV® TWA	0.5	1.0

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

HEALTH HAZARD INFORMATION

• Routes of exposure

Methyl mercaptan may cause adverse health effects following exposure via inhalation or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of methyl mercaptan by rats and mice caused restlessness, increased respiration, muscular weakness progressing to paralysis, convulsions, respiratory depression, deficient oxygenation of the blood (cyanosis), and death due to respiratory paralysis. Subchronic inhalation of methyl mercaptan by monkeys, rats, and mice caused altered blood chemistries in all three species, pulmonary edema in monkeys, and persistent hepatitis and cellular changes of the liver, lungs, and kidneys in mice.

2. *Effects on humans:* An accidental industrial exposure of a worker to methyl mercaptan caused elevated blood pressure, severe hemolytic anemia, methemoglobinemia, deep coma, and death due to pulmonary embolus 28 days following exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to methyl mercaptan can cause headache, dizziness, staggered gait, nausea, vomiting, pulmonary irritation, expiratory wheezing, rapid heart beat (tachycardia), rigidity of the arms and legs, bluish discoloration of the skin and mucous membranes (cyanosis), and irritation of the eyes and mucous membranes.

2. *Long-term (chronic):* Low-level exposure to methyl mercaptan can cause dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control 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 and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to methyl mercaptan, the physician 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 nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to methyl mercaptan at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin and respiratory system.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to methyl mercaptan. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

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

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of methyl mercaptan. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker)

should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

There are no NIOSH-validated sampling and analytical methods for methyl mercaptan. Direct reading devices calibrated to measure methyl mercaptan may be used if available.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with methyl mercaptan.

Workers should be provided with and required to use splash-proof safety goggles where liquid methyl mercaptan may come in contact with the eyes.

SANITATION

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

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with methyl mercaptan should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle methyl mercaptan should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to methyl mercaptan may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for methyl mercaptan

Operations	Controls
During use in the manufacture and processing of methyl mercaptan and methionine; during use as a catalyst or activator; during use in wood processing	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in the synthesis of chemical intermediates for the manufacture of resins, plastics, insecticides, and pressure-sensitive and oil-resistant adhesives	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as an odorant and warning agent in natural gas; during use in jet fuels; during the cleaning and maintenance of storage containers	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to methyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If methyl mercaptan gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to methyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If methyl mercaptan gets on the skin, wash it immediately with soap and water. If methyl mercaptan penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. 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.

SPILLS AND LEAKS

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

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

1. If methyl mercaptan is in the gaseous form, stop the flow of gas. If the source of the 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.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing methyl mercaptan, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood duct work is free from methyl mercaptan vapors. Burn the paper in a suitable location away from combustible material.
5. Large quantities of liquids containing methyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Methyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing methyl mercaptan may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

BIBLIOGRAPHY

- American Conference of Governmental Industrial Hygienists: *Air Sampling Instruments* (5th ed.), Cincinnati, 1978.
- American Conference of Governmental Industrial Hygienists: "Methyl Mercaptan," *Documentation of the Threshold Limit Values and Biological Exposure Indices* (5th ed.), Cincinnati, 1986.
- American Conference of Governmental Industrial Hygienists: *TLVs® Threshold Limit Values and Biological Exposure Indices for 1987-88*, Cincinnati, 1987.
- American Lung Association of San Diego and Imperial Counties: "Taking the Occupational History," *Annals of Internal Medicine*, 99:641-651, November 1983.
- Amoore, J.E., and Hautala, E.: "Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatilities for 214 Industrial Chemicals in Air and Water Dilution," *Journal of Applied Toxicology*, 3:272-290, 1983.
- Clayton, G.D., and Clayton, F.E. (eds.): *Toxicology*, Vol. IIA of *Patty's Industrial Hygiene and Toxicology* (3rd rev. ed.), John Wiley & Sons, Inc., New York, 1981.
- *Code of Federal Regulations*, U.S. Department of Labor, Occupational Safety and Health Administration, 29 CFR 1910.106, 1910.134, 1910.1000, OSHA 2206, revised July 1, 1986.
- *Code of Federal Regulations*, U.S. Department of Transportation, 49 CFR 172.101, Transportation 49, revised October 1, 1982.
- Goldman, R.H., and Peters, J.M.: "The Occupational and Environmental Health History," *Journal of the American Medical Association*, 246:2831-2836, 1981.
- Halperin, W.E., Ratcliffe, J., Frazier, T.M., Wilson, L., Becker, S.P., and Shulte, P.A.: "Medical Screening in the Workplace: Proposed Principles," *Journal of Occupational Medicine*, 28(8): 547-552, 1986.
- Hankinson, J.L.: "Pulmonary Function Testing in the Screening of Workers: Guidelines for Instrumentation, Performance, and Interpretation," *Journal of Occupational Medicine*, 28(10):1081-1092, 1986.
- Leidel, N.A., Busch, K.A., and Lynch, J.R.: *Occupational Exposure Sampling Strategy Manual*, U.S. Department of Health, Education, and Welfare, Public Health Service, Center

for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-173, Cincinnati, 1977.
• Levy, B.S., and Wegman, D.H. (eds.): *Occupational Health: Recognizing and Preventing Work-Related Disease*, Little, Brown and Company, Boston, 1983.
• Mark, H.F., Othmer, D.F., Overberger, C.G., Seaborg, G.T., Grayson, M., and Eckroth, D. (eds.): *Kirk-Othmer Encyclopedia of Chemical Technology* (3rd ed.), John Wiley & Sons, Inc., New York, 1981.
• National Fire Protection Association: *Fire Protection Guide on Hazardous Materials* (7th ed., 6th printing), Quincy, Massachusetts, 1978.
• National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control: *Criteria for a Recommended Standard. . . .Occupational Exposure to n-Alkane Mono Thiols, Cyclohexanethiol, Benzenethiol*, DHEW (NIOSH) Publication No. 78-213, 1978.
• National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control: *Registry of Toxic Effects of Chemical Substances* (Microfiche Edition), Sweet, D.V., and Lewis, R.J. (eds.), Cincinnati, April 1985.
• Proctor, N.H., and Hughes, J.P.: *Chemical Hazards of the Workplace*, J.B. Lippincott Company, Philadelphia, 1978.
• Rom, W.N. (ed.): *Environmental and Occupational Medicine*, Little, Brown and Company, Boston, 1983.
• Rothstein, M.A.: *Medical Screening of Workers*, Bureau of National Affairs, Washington, D.C., 1984.
• Rutstein, D.D., Mullan, R.J., Frazier, T.M., Halperin, W.E., Melius, J.M., and Sestito, J.P.: "Sentinel Health Events (Occupational): A Basis for Physician Recognition and Public Health Surveillance," *American Journal of Public Health*, 73:1054-1062, 1983.
• Scientific Assembly on Environmental and Occupational Health: "Evaluation of Impairment/Disability Secondary to Respiratory Disease," *American Review of Respiratory Diseases*, 126:945-951, 1982.
• Scientific Assembly on Environmental and Occupational Health: "Surveillance for Respiratory Hazards in the Occupational Setting," *American Review of Respiratory Diseases*, 126:952-956, 1982.

Table 3.—Respiratory protection for methyl mercaptan

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator
	Any self-contained breathing apparatus
	Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 12.5 ppm	Any supplied-air respirator operated in a continuous flow mode
	Any powered air-purifying respirator with organic vapor cartridge(s)
Less than or equal to 25 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s)
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 400 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 400 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 ppm (1.0 mg/m³) (ceiling).