

# Occupational Health Guideline for Methylene Chloride

## 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:  $\text{CH}_2\text{Cl}_2$
- Synonyms: Dichloromethane; methylene dichloride
- Appearance and odor: Colorless liquid with an odor like chloroform.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene chloride is 500 parts of methylene chloride per million parts of air (ppm) averaged over an eight-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for 5 minutes in any two-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 500 ppm averaged over a 15-minute period. NIOSH further recommends that permissible levels of methylene chloride be reduced where carbon monoxide is present. The NIOSH Criteria Document for Methylene Chloride should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Methylene chloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

### • Effects of overexposure

*1. Short-term Exposure:* Methylene chloride is an anesthetic. Inhaling the vapor may cause mental confusion,

light-headedness, nausea, vomiting, and headache. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and death. High vapor concentrations may also cause irritation of the eyes and respiratory tract. Exposure to this chemical may make the symptoms of angina worse. Skin exposure to the liquid may cause irritation. If the liquid is held in contact with the skin, it may cause skin burns. Splashes of the liquid into the eyes may cause irritation.

*2. Long-term Exposure:* Prolonged or repeated exposure to methylene chloride may cause irritation of the skin.

*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 methylene chloride.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to methylene chloride 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, cardiovascular system, and blood should be stressed. Clinical impressions of the autonomic nervous system and pulmonary function should be made, with additional tests conducted where indicated.

—Skin disease: Methylene chloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver function test: Methylene chloride causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Methylene chloride causes kidney damage in animals and this justifies special considera-

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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.

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tion before exposing persons with impaired renal function.

—Cardiovascular disease: Because of reports of excessive carbon monoxide levels following exposure to methylene chloride, persons with cardiac disease may be at increased risk.

—A complete blood count: A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Carboxyhemoglobin values should also be determined periodically, and any level above 5% should prompt an investigation of the worker and his workplace.

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

#### • Summary of toxicology

Methylene chloride vapor is a mild narcotic. Exposure of animals to 15,000 ppm for 7 hours was fatal. Animal experiments have shown that continuous exposure to 1,000 ppm can be lethal in 5 to 7 weeks for dogs and that fatty livers, icterus, pneumonia, and splenic atrophy developed in dogs. Cardiac arrhythmias attributed to sensitization of the myocardium have been observed following exposure to high concentrations of some chlorinated hydrocarbons, but dogs exposed to 10,000 and 20,000 ppm of methylene chloride did not show this phenomenon. In human experiments, inhalation of 500 to 1000 ppm for 1 to 2 hours resulted in lightheadedness; there was sustained elevation of carboxyhemoglobin level. High exposures have resulted in deaths in industrial situations. Lower but unknown concentrations have caused such symptoms as lightheadedness, weakness, nausea, and "drunken behavior," resulting in mistakes and accidental falls. Phosgene poisoning has been reported to occur in several cases where methylene chloride was used in the presence of an open fire. Liquid methylene chloride is irritating to the skin on repeated contact. Splashed in the eye, it is painfully irritating, but is not likely to cause serious injury.

## CHEMICAL AND PHYSICAL PROPERTIES

#### • Physical data

1. Molecular weight: 84.9
2. Boiling point (760 mm Hg): 39.8 C (104 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of methylene chloride): 2.9
5. Melting point: -97 C (-142 F)
6. Vapor pressure at 20 C (68 F): 350 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.32
8. Evaporation rate (butyl acetate = 1): 27.5

#### • Reactivity

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as

aluminum or magnesium powder, sodium and potassium may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving methylene chloride.

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

#### • Flammability

1. Flash point: None with normal test method
2. Autoignition temperature: 556 C (1033 F)
3. Flammable limits in air, % by volume: (at elevated temperatures) Lower: 12; Upper: 19
4. Extinguishant: Dry chemical, carbon dioxide, foam

#### • Warning properties

1. Odor Threshold: Different authors have reported varying odor thresholds for methylene chloride. Summer and May both report 150 ppm; Kirk-Othmer and Sax both report 25 to 50 ppm; Spector reports 320 ppm. Patty, however, states that since one can become adapted to the odor, it cannot be considered an adequate warning property.

2. Eye Irritation Level: Grant reports that methylene chloride "presents no particular hazard to the eyes." Kirk-Othmer, however, reports that "methylene chloride vapor is seriously damaging to the eyes." Sax agrees with Kirk-Othmer's statement.

The *Documentation of TLV's* states that irritation of the eyes has been observed in workers who had been exposed to concentrations up to 5000 ppm, but that neurasthenic disorders were found in 50% and digestive disturbances in 30% of the persons exposed.

3. Other Information: Gleason reports that methylene chloride may be "irritating to the respiratory tract and may produce pulmonary edema" but gives no quantitative information. The *Documentation of TLV's* reports that in one investigation, irritation of the respiratory passages was observed in workers who had been exposed to concentrations up to 5000 ppm.

4. Evaluation of Warning Properties: Since no detailed information is available relating the irritant effects of methylene chloride to air concentrations and since adaptation to the odor occurs, methylene chloride is treated as a material with poor warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

#### • Eight-Hour Exposure Evaluation

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).

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene chloride. 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.

### • Peak Above Ceiling Evaluation

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of methylene chloride. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three 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 methylene chloride may be used. An analytical method for methylene chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## 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 methylene chloride.
- Non-impervious clothing which becomes wet with liquid methylene chloride should be removed promptly and not reworn until the methylene chloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylene chloride may contact the eyes.

## SANITATION

- Skin that becomes wet with liquid methylene chloride should be promptly washed or showered with soap or mild detergent and water to remove any methylene chloride.

## COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a solvent in paint and varnish removers; manufacture of aerosols; cold cleaning and ultrasonic cleaning; and as an extraction solvent for foods and furniture processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a cooling solvent in manufacture of cellulose acetate; in organic synthesis; and in plastics processing	Process enclosure; local exhaust ventilation
Use as a solvent in vapor degreasing of thermal switches and thermometers	Process enclosure; local exhaust ventilation
Use as a secondary refrigerant in air conditioning and scientific testing	General dilution ventilation; local exhaust ventilation; personal protective equipment

## Operation

Use as an extraction solvent for edible fats, coca, butter, beer flavoring in hops, decaffeinated coffee, oleoresin manufacture, oils, waxes, perfumes, flavorings, and drugs

Use as a solvent for paints, lacquers, varnishes, enamels, adhesives, rubber cements, manufacture of printed circuit boards, as a carrier for pharmaceutical tablet coatings, shrink-fitting of synthetic rubber covers, and dyeing of synthetic fibers

## Controls

General dilution ventilation; local exhaust ventilation; personal protective equipment

General dilution ventilation; local exhaust 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 methylene chloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

### • Skin Exposure

If methylene chloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water if the methylene chloride has not already evaporated. If methylene chloride soaks through the clothing, remove the clothing promptly 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 methylene chloride, 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 methylene chloride 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 AND LEAK PROCEDURES

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

• If methylene chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

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## RESPIRATORY PROTECTION FOR METHYLENE CHLORIDE

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### Condition

### Minimum Respiratory Protection\* Required Above 500 ppm

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#### Vapor Concentration

5000 ppm or less

Any supplied-air respirator with a full facepiece, helmet, or hood.

Any self-contained breathing apparatus with a full facepiece.

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Greater than 5000 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.

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#### Fire Fighting

Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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#### Escape

Any gas mask providing protection against organic vapors.

Any escape self-contained breathing apparatus.

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

