Occupational Health Guideline for Methyl 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:** CH₂Cl
- **Synonyms:** Chloromethane
- **Appearance and odor:** Colorless gas with a faint, sweet odor that is not noticeable at dangerous concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl chloride is 100 parts of methyl chloride per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and a maximum acceptable peak of 300 ppm for 5 minutes in any three-hour period. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl chloride from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**
  Methyl chloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.
- **Effects of overexposure**
  1. **Short-term Exposure:** Deaths have occurred following single severe or repeated prolonged moderate overexposure. Overexposure may cause dizziness, vomiting, abdominal pain, diarrhea, breathing difficulties, and unconsciousness. Convulsions and disturbances of vision may occur. It may also damage the kidneys, liver, or blood. The symptoms of methyl chloride overexposure are usually delayed in onset. Frostbite may occur from contact with liquefied methyl chloride.
  2. **Long-term Exposure:** Repeated moderate or mild overexposure may cause delayed (24 to 48 hours) onset of dizziness, headache, mental confusion, slurred speech, double vision, and sleepiness. Recovery from the effects of exposure to this chemical may be slow.
  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 chloride.

- **Recommended medical surveillance**
  The following medical procedures should be made available to each employee who is exposed to methyl 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 exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver, and kidneys should be stressed.
  2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.
- **Summary of toxicology**
  Methyl chloride vapor is a narcotic and may cause a toxic encephalopathy. The LC50 for mice for 7-hour exposure was approximately 3000 ppm. At this concentration, some species showed pulmonary edema with hemorrhage, moderate centrolobular necrosis of the liver, and tubular damage in the kidney. At 500 ppm repeated daily for 6 hours, there was response in some species, while 300 ppm daily for 64 weeks produced no detectable effects. Human fatalities have occurred from a single severe exposure or less severe prolonged exposures. Severe but nonfatal poisoning in man is characterized by a latent period of several hours, followed by dizziness, nausea, vomiting, double vision, weakness, paralysis, convulsions, and coma; renal or hepatic

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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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**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

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damage and anemia also occur. Some workers exposed
daily to concentrations averaging 195 to 475 ppm
showed delayed signs, including weakness, drowsiness,
sluggish gait, slurred speech, lapses of memory, and
cyanosis. The onset is often insidious and may be
confused with mild viral illness; more severe intoxica-
tion has been mistaken for viral encephalitis or heavy-
metal poisoning. Effects may last for a long period
following exposure. No effects were seen in other
workers exposed to 15 to 195 ppm. Frostbite may result
from contact with the liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data
  1. Molecular weight: 50.5
  2. Boiling point (760 mm Hg): $-24.2 \, ^\circ\text{C}$ ($-11.6 \, ^\circ\text{F}$)
  3. Specific gravity (water = 1): 0.92 (liquid)
  4. Vapor density (air = 1 at boiling point of methyl
     chloride): 1.8
  5. Melting point: $-97.6 \, ^\circ\text{C}$ ($-144 \, ^\circ\text{F}$)
  6. Vapor pressure at 20 C (68 F): 4.8 atm.
  7. Solubility in water, g/100 g water at 20 C (68 F):
     Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable

- Reactivity
  1. Conditions contributing to instability: Heat, espe-
cially when in contact with water or metals such as
     aluminum, magnesium, and zinc.
  2. Incompatibilities: Contact with chemically active
     metals such as potassium, powdered aluminum, magne-
     sium, and zinc will cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases
     and vapors (such as hydrogen chloride and carbon
     monoxide) may be released in a fire involving methyl
     chloride.
  4. Special precautions: Methyl chloride will attack
     some forms of plastics, rubber, and coatings.

- Flammability
  1. Flash point: Not pertinent (gas)
  2. Autoignition temperature: 632 C (1170 F)
  3. Flammable limits in air, % by volume: Lower: 7.6;
     Upper: 19

- Warning properties
  May report an odor threshold of 10 ppm. However,
Patty states that methyl chloride has no odor or other
warning properties, and Jacobs states that methyl chlo-
ride does not have adequate warning properties at
higher concentrations.
Methyl chloride is not an eye irritant, according to
Grant, even in concentrations which are “dangerously
toxic.”

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 methyl chloride. Each mea-
surement 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 methyl chloride. Each mea-
surement should consist of a 5-minute sample or a series
of consecutive samples totalling 5 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 methyl chloride on activated carbon, followed by
desorption with methanol and gas chromatographic
analysis. Also, detector tubes certified by NIOSH under
42 CFR Part 84 or other direct-reading devices calibrat-
ed to measure methyl chloride may be used. An analyc-
tical method for methyl chloride is in the NIOSH
Manual of Analytical Methods, 2nd Ed., Vol. 4, 1978,
available from the Government Printing Office, Wash-
ington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that
  engineering controls be used to reduce environmental
  concentrations to the permissible exposure level. How-
ever, 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 the skin from becoming wet with liquid methyl chloride or from becoming frozen from contact with vessels containing methyl chloride.
- Any clothing which becomes wet with liquid methyl chloride should be removed immediately and not reworn until the methyl chloride has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl chloride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use in manufacture of silicone resins, and tetramethyl lead; use as a methylating and chlorinating agent; use as a dewatering agent in petroleum refining; use as a catalyst solvent in production of butyl rubber</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use in synthesis of a variety of other compounds; as an extractant for greases, oils, and resins</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Liberation during use as a foaming agent in production of plastics; in the manufacture and application of pesticides, pharmaceuticals, and perfumes; as a propellant in aerosols; and use as a refrigerant</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
</tbody>
</table>

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 liquefied methyl chloride gets into the eyes, wash eyes immediately with large amounts of water. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
- **Skin Exposure**
  If liquefied methyl chloride gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water if the methyl chloride has not already evaporated. If liquefied methyl chloride soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.
- **Breathing**
  If a person breathes in large amounts of methyl 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.
- **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.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If methyl chloride is leaked, the following steps should be taken:
  1. Remove all ignition sources.
  2. Ventilate area of leak.
- Waste disposal method:
  Methyl chloride may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- Ansul Chemical Company: *Physical Effects of Methyl*
Chloride.

## RESPIRATORY PROTECTION FOR METHYL CHLORIDE

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 100 ppm</th>
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<tbody>
<tr>
<td><strong>Vapor Concentration</strong></td>
<td></td>
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<tr>
<td>1000 ppm or less</td>
<td>Any supplied-air respirator.</td>
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<tr>
<td></td>
<td>Any self-contained breathing apparatus.</td>
</tr>
<tr>
<td>5000 ppm or less</td>
<td>Any supplied-air respirator with a full facepiece, helmet, or hood.</td>
</tr>
<tr>
<td></td>
<td>Any self-contained breathing apparatus with a full facepiece.</td>
</tr>
<tr>
<td>10,000 ppm or less</td>
<td>A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.</td>
</tr>
<tr>
<td>Greater than 10,000 ppm or entry and escape from unknown concentrations</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td></td>
<td>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.</td>
</tr>
<tr>
<td><strong>Fire Fighting</strong></td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td><strong>Escape</strong></td>
<td>Any escape self-contained breathing apparatus.</td>
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</tbody>
</table>

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