Occupational Health Guideline for Methylal

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: CH₃OCH₂OCH₃
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetel formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- Routes of exposure
  Methylal can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.
- Effects of overexposure
  1. Short-term Exposure: Overexposure to methylal may cause irritation of the eyes, nose, and throat, light-headedness, incoordination, and unconsciousness.
  2. Long-term Exposure: Prolonged overexposure to methylal 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 methylal.
- Recommended medical surveillance
  The following medical procedures should be made available to each employee who is exposed to methylal at potentially hazardous levels:
  1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylal exposure.
     - Skin disease: Methylal is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.
     - Liver disease: Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.
     - Kidney disease: Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.
  2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.
- Summary of toxicology
  Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC₅₀ level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

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

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Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data
  1. Molecular weight: 76
  2. Boiling point (760 mm Hg): 44 C (111 F)
  3. Specific gravity (water = 1): 0.86
  4. Vapor density (air = 1 at boiling point of methylal): 2.6
  5. Melting point: –105 C (–157 F)
  6. Vapor pressure at 20 C (68 F): 330 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 33
  8. Evaporation rate (butyl acetate = 1): 23.1
- Reactivity
  1. Conditions contributing to instability: Heat, presence of acids
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
- Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.
  - Flammability
    1. Flash point: –18 C (–4 F) (closed cup)
    2. Autoignition temperature: 237 C (459 F)
    3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
  - Extinguisher: Dry chemical, alcohol foam, carbon dioxide
- Warning properties
  1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
  2. Eye Irritation Level: Grant states that “exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause... occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina.”

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, 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
  Sampling and analyses may be performed by collection of methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal is in the NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

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

- Any clothing which becomes wet with liquid methylal should be removed immediately and not re-worn until the methylal is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

**SANITATION**

- Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

**COMMON OPERATIONS AND CONTROLS**

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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
</tr>
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<tbody>
<tr>
<td>Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxyacids</td>
<td>General dilution ventilation; process enclosure; personal protective equipment</td>
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<tr>
<td>Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines</td>
<td>General dilution ventilation; process enclosure; personal protective equipment</td>
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<tr>
<td>Use as a reaction solvent with acetylene or in Grignard and Repp reaction; use as a source of formaldehyde and methanol</td>
<td>General dilution ventilation; process enclosure; personal protective equipment</td>
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<tr>
<td>Use as a methylating agent or chemical intermediate</td>
<td>General dilution ventilation; process enclosure; personal protective equipment</td>
</tr>
<tr>
<td>Use in manufacture of perfume</td>
<td>General dilution ventilation; process enclosure; personal protective equipment</td>
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</tbody>
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- **Eye Exposure**
  If methylal 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 methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

- **Breathing**
  If a person breathes in large amounts of methylal, 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 methylal 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 methylal is spilled or leaked, the following steps should be taken:**
  1. Remove all ignition sources.
  2. Ventilate area of spill or leak.
  3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
• Waste disposal method:
Methylal may be disposed of by dissolving in alcohol of
greater molecular weight than butyl alcohol and atom-
izing in a suitable combustion chamber.

REFERENCES
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Journal of Industrial Medicine, 8:279-283, 1951.

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RESPIRATORY PROTECTION FOR METHYLAL

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 1000 ppm</th>
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<tr>
<td>Vapor Concentration</td>
<td>Any supplied-air respirator. Any self-contained breathing apparatus.</td>
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<tr>
<td>10,000 ppm or less</td>
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<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. 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>
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<tr>
<td>Fire Fighting</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>Escape</td>
<td>Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.</td>
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*Only NIOSH-approved or MSHA-approved equipment should be used.