# OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR MONOMETHYL HYDRAZINE

# POTENTIAL HUMAN CARCINOGEN

## INTRODUCTION

This guideline summarizes pertinent information about monomethyl hydrazine 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 Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.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:** $CH_6N_2$
- **Structure:** $CH_3NHNH_2$
- **Synonyms:** Hydrazomethane, 1-methyl hydrazine, methyl hydrazine, MMH
- **Identifiers:** CAS 60-34-4; RTECS MV5600000; DOT 1244, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Colorless liquid with a strong ammonia-like odor

## CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46.09
2. Boiling point (at 760 mmHg): 87.5°C (189°F)
3. Specific gravity (water = 1): 0.874
4. Vapor density (air = 1 at boiling point of monomethyl hydrazine): 1.59
5. Melting point: -52.4°C (-61.6°F)
6. Vapor pressure: At 20°C (68°F): 36.0 mmHg; at 25°C (77°F), 49.6 mmHg
7. Soluble in water
8. Evaporation rate (butyl acetate = 1): 1.5
9. Saturation concentration in air (approximate) at 25°C (77°F): 6.5% (65,300 ppm)
10. Ionization potential: 7.67 eV

- **Reactivity**

Incompatibilities: Monomethyl hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.

Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving monomethyl hydrazine.

Caution: Monomethyl hydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -8.3°C (17°F) (closed cup)
2. Autoignition temperature: 194°C (382°F)
3. Flammable limits in air, % by volume: Lower, 2.5; upper, 92
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Monomethyl hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

1. Odor threshold: 1-3 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

## EXPOSURE LIMITS

The Current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for monomethyl hydrazine is 0.2 parts of monomethyl hydrazine per million parts of air (ppm) [0.35 milligrams of monomethyl hydrazine per cubic meter of air ($mg/m^3$)] as a ceiling concentration which shall at no time be exceeded (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that monomethyl hydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is

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0.04 ppm (0.08 mg/m³) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated monomethyl hydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value ceiling (TLV®-C), the concentration that should not be exceeded during any part of the working exposure, of 0.2 ppm (0.35 mg/m³) (Skin) (Table 1).

**Table 1.—Occupational exposure limits for monomethyl hydrazine**

| | Exposure limits ppm | mg/m³ |
|---|---|---|
| OSHA PEL | | |
| Ceiling (Skin)* | 0.2 | 0.35 |
| NIOSH REL (Ca)† | | |
| Ceiling (120 min) | 0.04 | 0.08 |
| ACGIH TLV® (A2)§ | | |
| Ceiling (Skin) | 0.2 | 0.35 |

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

## HEALTH HAZARD INFORMATION

**• Routes of exposure**

Monomethyl hydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

**• Summary of toxicology**

*Effects on animals:* Acute inhalation of monomethyl hydrazine by dogs caused respiratory irritation, pulmonary hemorrhage and edema, central nervous system stimulation, and convulsions; acute subcutaneous injection in dogs caused damage to the kidneys (including hemoglobinuria, hyaline droplet degeneration, and severe renal epithelial damage). Subchronic inhalation of monomethyl hydrazine by dogs, monkeys, rats, or mice produced nose and eye irritation, diarrhea, rapid respiration, deficient oxygenation of the blood (cyanosis), impaired muscular coordination (ataxia), tremors, convulsions, blood disorders (including significant hemolysis and hemolytic anemia), increased storage of iron in the body (hemosiderosis), and reduced bile flow (cholestasis). Chronic oral administration of monomethyl hydrazine to mice produced lung tumors; hamsters similarly exposed developed liver cancer.

**• Signs and symptoms of exposure**

*Short-term (acute):* Monomethyl hydrazine can cause irritation of the eyes and respiratory tract, nausea, diarrhea, and convulsions.

## 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 monomethyl hydrazine, 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 eyes, liver, kidneys, and hematopoietic (blood-cell-forming), respiratory, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

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 monomethyl hydrazine 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 liver, kidneys, and hematopoietic and respiratory systems. The physician should obtain baseline values for liver function tests. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to monomethyl hydrazine.

• **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 monomethyl hydrazine. 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 integrity and physiologic function of the eyes, liver, kidneys, and hematopoietic, respiratory, and central nervous 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 ATS: standardized questionnaires and lung function tests.

• **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. Because occupational exposure to monomethyl hydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

## MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of monomethyl hydrazine. 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 120-minute sample or a series of consecutive samples that total 120 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**
Sampling and analysis may be performed by collecting monomethyl hydrazine vapors with sulfuric-acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure monomethyl hydrazine may also be used if available. A detailed sampling and analytical method for monomethyl hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

## 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, and other appropriate protective clothing necessary to prevent skin contact with monomethyl hydrazine.

## SANITATION

Clothing which is contaminated with monomethyl hydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of monomethyl hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of monomethyl hydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with monomethyl hydrazine 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 monomethyl hydrazine 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 monomethyl hydrazine may occur and control methods which may be effective in each case are listed in Table 2.

## 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 monomethyl hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If monomethyl hydrazine 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.

**Table 2.—Operations and methods of control for monomethyl hydrazine**

| Operations | Controls |
|---|---|
| During use in the preparation and handling of liquid rocket propellants; during use as a chemical intermediate for the synthesis of pesticides | Process enclosure, local exhaust ventilation, personal protective equipment |
| During use in polymer technology and in miscellaneous processes such as electroplating, etching, and photographic processing | Process enclosure, local exhaust ventilation, personal protective equipment |
| During the manufacture and distribution of monomethyl hydrazine; during maintenance of storage containers | Process enclosure, local exhaust ventilation, personal protective equipment |

• **Skin exposure**

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

If monomethyl hydrazine gets on the skin, wash it immediately with soap and water. If monomethyl hydrazine 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 monomethyl hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing monomethyl hydrazine may be flushed with water; the waste water may then be collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing monomethyl hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Monomethyl hydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

## 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.**

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## Table 3.—Respiratory protection for monomethyl hydrazine

| Condition | Minimum respiratory protection* |
|---|---|
| Any detectable concentration | 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 |
| Planned or emergency entry into environments containing unknown or any detectable concentration | 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 appropriate escape-type self-contained breathing apparatus |

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