

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** MONOMETHYL HYDRAZINE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for MONOMETHYL HYDRAZINE

The basic text of this document contains the draft technical standard approved by the Joint Review Committee of the NIOSH/OSHA Standards Completion Program and the supporting documentation for the substance MONOMETHYL HYDRAZINE.

The SCP draft technical standards are recommendations to the Department of Labor for its consideration in rulemaking and have no legal status until final rules have been promulgated by that agency. This draft standard is provided for your information only.

The References and Sources, Respirator Table Documentation and Use/Exposure and Control Documentation are the working documents used by the various SCP working groups during the development of the draft technical standard and serve as the technical foundation for the standard. The classification for each substance and the regulatory statements were derived following a decision logic established for the various sections of the standard.

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(a) Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of monomethyl hydrazine not in excess of 0.2 parts per million (ppm) (0.35 milligrams per cubic meter, (mg/m³)) averaged over any 15-minute period during an eight-hour work shift, as stated in § 1910.1000, Table Z-1.

(2) "Action level" means one half of the permissible exposure for monomethyl hydrazine.

(b) Exposure determination and measurement. (1) Each employer who has a place of employment in which monomethyl hydrazine is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of monomethyl hydrazine at or above the action level. The determination shall be made each time there is a change in increase in airborne concentrations of monomethyl hydrazine.

(2) A written record of the determination shall be made and it shall contain at least the following information:

(i) Any information, observations, or calculations which may indicate employee exposure to monomethyl hydrazine;

(ii) Any measurements of monomethyl hydrazine taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to monomethyl hydrazine; and

(iv) Date of determination, work being performed at the time, location within work site, name, and social security number of each employee considered.

(3) If the employer determines that any employee may be exposed to monomethyl hydrazine at or above the action level, the exposure of the employee in each work operation who is believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum eight-hour time weighted average exposure of the employee.

(4) If the exposure measurement taken pursuant to paragraph (b)(3) of this section reveals employee exposure to monomethyl hydrazine at or above the action level, the employer shall:

(i) Identify all employees who may be exposed at or above the action level; and

(ii) Measure the exposure of the employees so identified.

(5) If an employee exposure measurement reveals that an employee is exposed to monomethyl hydrazine at or above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every two months.

(6) If an employee exposure measurement reveals that an employee is exposed to monomethyl hydrazine above the permissible exposure, the employer shall:

(i) Measure the exposure monthly of the employee so exposed;

(ii) Institute control measures as required by paragraph (d) of this section; and

(iii) Individually notify, in writing, within five days, every employee who is found to be exposed to monomethyl hydrazine above the permissible exposure. The employee shall also be notified of the corrective action being taken to reduce the exposure to at or below the permissible exposure.

(7) If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to monomethyl hydrazine

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below the action level, the employer may terminate measurement for the employee.

(8) For purposes of this paragraph, employee exposure is that which would occur if the employee were not using a respirator.

(c) Methods of measurement. (1) An employee's exposure shall be obtained by any combination of long term or short term samples which represents the employee's actual exposure averaged over the time periods appropriate to the permissible exposure (SEE APPENDIX B (iv) of this section).

(2) The method of measurement shall have an accuracy, to a confidence level of 95 percent, of not less than that given in Table 1.

Table 1

Concentration	Required Accuracy
Above permissible exposure	$\pm 25\%$
At or below permissible exposure and above the action level	$\pm 35\%$
At or below the action level	$\pm 50\%$

(d) Compliance. (1) No employee shall be exposed to monomethyl hydrazine above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of monomethyl hydrazine shall be controlled to at or below the permissible exposure by engineering and work practice controls:

(i) Engineering and work practice controls shall be instituted to reduce exposures to at or below the permissible exposure, except to the extent that such controls are not technically feasible.

(ii) Wherever engineering and work practice controls are not sufficient to reduce exposures to at or below the permissible exposure, they shall nonetheless be used to reduce exposure to the lowest level feasible and shall be supplemented by respirators in accordance with paragraph (d)(4) of this section.

(3) Engineering controls. (i) When mechanical ventilation is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity, static pressure, or air volume, shall be made at least every three months. Measurements of system effectiveness shall also be made within five days of any change in production, process, or control which might result in an increase in airborne concentrations of monomethyl hydrazine.

(ii) In the design of open-surface tank ventilation for the purposes of § 1910.94(d), operations involving monomethyl hydrazine shall be classified as A-1 at 70 degrees F (21 degrees C).

(4) Compliance with the permissible exposure shall not be achieved by the use of respirators except:

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- (i) During the time period necessary to install or implement engineering or work practice controls; or
 - (ii) In work situations in which engineering and work practice controls are technically not feasible; or
 - (iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of monomethyl hydrazine to at or below the permissible exposure; or
 - (iv) For operations which require entry into tanks or closed vessels; or
 - (v) In emergencies.
- (5) Where respirators are needed and permitted under this paragraph to reduce employee exposure, the employer shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.

TABLE 2 RESPIRATORY PROTECTION FOR MONOMETHYL HYDRAZINE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION

Vapor Concentration	
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet or hood. ----- Any self-contained breathing apparatus with a full facepiece. -----
Greater than 5 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. (Supplied-air suits may be necessary.) -----
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. -----
Escape	Any gas mask with full facepiece providing protection against monomethyl hydrazine. -----

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Any escape self-contained breathing apparatus with full facepiece.

(6) Respirators shall be approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) or by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

(7) The employer shall institute a respiratory protection program in accordance with § 1910.134(b), (d), (e), and (f).

(e) Fire and safety. (1) The employer shall familiarize himself with the information contained in the Substance Technical Guidelines (Appendix B of this section) for monomethyl hydrazine.

(2) For the purpose of compliance with § 1910.309, locations classified as hazardous locations due to the presence of monomethyl hydrazine shall be Class I, Group C.

(3) For the purpose of compliance with § 1910.157, monomethyl hydrazine is classified as a Class B fire hazard.

(4) For the purpose of compliance with § 1910.178, locations classified as hazardous locations due to the presence of monomethyl hydrazine shall be Class I, Group C.

(5) For the purpose of compliance with § 1910.106, liquid monomethyl hydrazine is classified as a Class IB flammable liquid.

(6) Dip tank operations shall be performed in accordance with §§ 1910.108 and 1910.94(d).

(7) Where a fan is located in ductwork and where monomethyl hydrazine is present in the ductwork in concentrations greater than 6300 ppm (approximately 25% of the lower flammable limit), the fan rotating element shall be of nonsparking material or the casing shall consist of, or be lined with, nonsparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.

(8) Sources of ignition such as smoking or open flames are prohibited where monomethyl hydrazine is handled, used or stored.

(9) Monomethyl hydrazine shall be stored so as not to come in contact with oxidizers, oxides of iron and copper, manganese, lead, and copper and its alloys. Anhydrous monomethyl hydrazine shall be stored under a nitrogen atmosphere.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use impervious clothing, gloves, face shields (eight-inch minimum) and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid monomethyl hydrazine. Face shields shall comply with § 1910.133 (a)(2), (a)(4), (a)(5), and (a)(6).

(2) Employers shall ensure that clothing contaminated with monomethyl hydrazine is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of monomethyl hydrazine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the monomethyl hydrazine, the employer shall inform the person performing the operation of the hazardous properties of monomethyl hydrazine.

(3) Where there is any possibility of exposure of an employee's body to liquid monomethyl hydrazine, employers shall provide facilities for quick drenching of the body within the immediate work area for emergency use.

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(4) Employers shall ensure that any clothing which becomes wet with or non-impervious clothing which becomes contaminated with monomethyl hydrazine be removed immediately and not reworn until the monomethyl hydrazine is removed from the clothing.

(5) Employers shall provide and ensure that employees use splash-proof safety goggles (cup-cover type dust and splash safety goggles) which comply with § 1910.133 (a)(2)-(a)(6) where there is any possibility of liquid monomethyl hydrazine contacting the eyes.

(6) Where there is any possibility that an employee's eyes may be exposed to liquid monomethyl hydrazine, employers shall provide an eye-wash fountain within the immediate work area for emergency use.

(g) Spills and disposal. (1) In the event that liquid monomethyl hydrazine is spilled the employer shall immediately eliminate potential sources of ignition, provide available ventilation and then clean up the spill.

(2) Liquid monomethyl hydrazine shall not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

(h) Sanitation. (1) Employers shall ensure that employees whose skin becomes contaminated with monomethyl hydrazine immediately wash or shower to remove any monomethyl hydrazine from the skin.

(2) Employers shall ensure that employees do not eat or smoke in areas where liquid monomethyl hydrazine is handled, processed or stored.

(3) Employers shall ensure that employees who handle liquid monomethyl hydrazine wash their hands thoroughly before eating, smoking or using toilet facilities.

(i) Training and information. (1) Each employer who has a workplace in which monomethyl hydrazine is present shall keep a copy of this regulation with Appendixes A, B and C at the workplace. This material shall be made readily available to affected employees.

(2) Each employer who has employees exposed to monomethyl hydrazine above the action level or employees who may have skin or eye contact with liquid monomethyl hydrazine, or employees who work where monomethyl hydrazine presents a fire or explosion hazard, shall annually:

(i) Inform affected employees of the information contained in the Substance Safety Data Sheet for monomethyl hydrazine (Appendix A of this section);

(ii) Advise affected employees as to the signs and symptoms of exposure to monomethyl hydrazine.

(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of exposure to monomethyl hydrazine which are listed in Appendix A of the section;

(v) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to monomethyl hydrazine.

(j) Medical Surveillance. (1) The employer shall provide medical procedures as required by this paragraph. All medical procedures shall be performed by or under the supervision of a physician at no cost to the employee.

(2) The employer shall make available to each employee who is to be exposed to liquid monomethyl hydrazine or airborne concentrations of monomethyl hydrazine at or above the action level, a medical examination which shall include the following:

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(i) A medical history and physical examination with emphasis on central nervous system, liver, blood, respiratory system, cardiovascular system and eyes.

(ii) A complete blood count to include a red and white cell count, a differential smear, hemoglobin and hematocrit.

(iii) A profile of liver function.

(iv) 14" x 17" chest roentgenogram.

(v) Pulmonary function testing, FVC and FEV (1 sec).

(3) The employer shall obtain from the physician, as a record of the examination, the following information:

(i) A written opinion which conforms with paragraph (j)(7) of this section.

(ii) A record of the results of the complete blood count.

(iii) A record of the results of liver function tests.

(iv) 14" x 17" chest roentgenogram or a medically acceptable copy.

(v) A record of the results of the pulmonary function testing.

(4) The employer shall make available to each employee, exposed to monomethyl hydrazine in excess of the action level at 12 months from the date of the employee's first exposure, and at every 12 months of exposure in excess of the action level thereafter, a medical examination which must include the following:

(i) A medical history and physical examination with emphasis on central nervous system, liver, blood, respiratory system, cardiovascular system and eyes.

(ii) A complete blood count to include a red and white cell count, a differential smear, hemoglobin and hematocrit.

(iii) A profile of liver function.

(iv) 14" x 17" chest roentgenogram when indicated by results of pulmonary function testing.

(v) Pulmonary function testing, FVC and FEV (1 sec).

(5) The employer shall obtain from the physician, as a record of the periodic examination, the following information:

(i) A written opinion which conforms with paragraph (j)(7) of this section.

(ii) A record of the results of the complete blood count.

(iii) A record of the results of the liver function tests.

(iv) 14" x 17" chest roentgenogram or a medically acceptable copy.

(v) A record of the results of the pulmonary function testing.

(6) The employer shall provide to the examining physician the following information:

(i) A copy of this regulation with its Appendixes A, B, and C for monomethyl hydrazine;

(ii) A description of the employee's duties as they relate to his exposure to monomethyl hydrazine;

(iii) A description of any personal protective equipment and respirators required to be used;

(iv) The results of any measurement which may indicate the affected employee's exposure;

(v) The affected employee's anticipated exposure; and

(vi) Upon request of the physician, any available information from previous medical examination of the affected employee.

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(7)(i) The physician's written opinion shall be a signed statement by the examining physician specifically stating: (A) Whether the employee has any detected medical condition which would place the employee at increased risk of material impairment of the employee's health from exposure to monomethyl hydrazine or would directly or indirectly aggravate any detected medical condition;

(B) Any recommended limitations upon the employee's exposure to monomethyl hydrazine, including limitations upon the use of personal protective equipment and respirators;

(C) That the employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.

(ii) The physician's written opinion shall not reveal specific medical findings or diagnoses unrelated to exposure to monomethyl hydrazine.

(iii) The employer shall provide the employee with a copy of the physician's written opinion.

(8) No employee shall be exposed to liquid monomethyl hydrazine or airborne concentrations of monomethyl hydrazine in such a way as would put the employee at increased risk of material impairment of his health from such exposure. This determination may be based on the physician's written opinion.

(9) The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to monomethyl hydrazine.

(10) If the examining physician chooses to use alternative medical examinations to those specified in paragraphs (j)(2) and (4) of this section, the employer may accept such alternative medical surveillance examinations as meeting the requirements of this part provided that the employer:

(i) Obtains a statement from the examining physician setting forth the alternative medical examinations and the rationale for substitution and evidence that they will be equally effective.

(ii) Informs each exposed employee of the fact that alternative medical examinations to those required in paragraphs (j)(2) or (4) of this section are to be made available.

(11) If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risks involved by refusing to be examined.

(12) No medical procedure which would be performed pursuant to this section need be performed if records of a previous such procedure performed within the past three months are acceptable to the examining physician.

(k) Recordkeeping. (1) Exposure determination. (i) The employer shall keep an accurate record of all determinations required to be made pursuant to paragraph (b)(1) of this section.

(ii) This record shall include the written determination required in paragraph (b)(2) of this section.

(iii) This record shall be maintained until replaced by a more recent record.

(2) Exposure measurements. (i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to monomethyl hydrazine.

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- (ii) This record shall include:
 - (A) The date of measurement;
 - (B) Operations involving exposure to monomethyl hydrazine which are being monitored;
 - (C) Sampling and analytical methods used and evidence of their accuracy, including the method, results and date of calibration of sampling equipment;
 - (D) Number, duration, and results of samples taken; and
 - (E) Name, social security number and exposure of the employee monitored.
- (iii) This record shall be maintained until replaced by a more recent record but in no event for less than one year.
- (3) Mechanical ventilation. (i) When mechanical ventilation is used as an engineering control, the employer shall maintain an accurate record of the measurements demonstrating the effectiveness of such ventilation required by paragraph (d)(3) of this section.
 - (ii) This record shall include:
 - (A) Date of measurement;
 - (B) Type of measurement taken;
 - (C) Result of measurement.
 - (iii) These records shall be maintained for at least one year.
- (4) Employee training and information. (i) The employer shall keep an accurate record of all employee training and information required by paragraph (i) of this section.
 - (ii) This record shall include:
 - (A) Date of training;
 - (B) Name and social security number of employee trained;
 - (C) Content or scope of training provided.
 - (iii) This record shall be maintained until replaced by a more recent record.
- (5) Medical surveillance. (i) The employer shall keep an accurate record of employee medical surveillance required by paragraph (j) of this section.
 - (ii) This record shall include:
 - (A) Information concerning medical conditions obtained from the employee pursuant to paragraph (j)(2) of this section;
 - (B) Any employee medical complaints relative to exposure to monomethyl hydrazine;
 - (C) A copy of information provided to the physician pursuant to paragraph (j)(4)(ii), (iii), (iv), (v), and (vi) of this section.
 - (D) Physician's written opinion; and
 - (E) A signed statement of any refusal to be examined.
 - (iii) This record shall be maintained for the duration of the employment of the affected employee.
- (6) Access to records. (i) All records required to be maintained by this section shall be made available upon request to authorized representatives of the Assistant Secretary of Labor for Occupational Safety and Health and the Director of the National Institute for Occupational Safety and Health.
 - (ii) Employee exposure determination and exposure measurement records required to be maintained by this section shall be made available to employees and former employees and their designated representatives.

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(iii) Employee medical records required to be maintained by this section shall be made available upon written request to a physician designated by the employee or former employee.

(1) Employee observation of measurement. (1) The employer shall give affected employees or their representatives an opportunity to observe any measurement of employee exposure to monomethyl hydrazine which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to monomethyl hydrazine requires entry into an area where the use of personal protective devices, including respirators, is required, the observer shall be provided with and required to use such equipment and comply with all other applicable safety procedures.

(3) Without interfering with the measurement, observers shall be entitled to:

(i) Receive an explanation of the measurement procedure.

(ii) Visually observe all steps related to the measurement of the airborne concentration of monomethyl hydrazine that are being performed at the place of exposure; and

(iii) Record the results obtained.

NOTE: The information contained in the following appendixes is advisory in nature and is not intended, by itself, to create any additional obligations not otherwise imposed or detract from any existing obligation.

APPENDIX A

SUBSTANCE SAFETY DATA SHEET
FOR MONOMETHYL HYDRAZINE

I. SUBSTANCE IDENTIFICATION

A. Substance: Monomethyl hydrazine

B. Permissible Exposure: 0.2 parts of monomethyl hydrazine per million parts of air (ppm) (0.35 milligrams of monomethyl hydrazine per cubic meter of air, (mg/m³)) shall not be exceeded during any 8-hour work shift.

C. Appearance and Odor: Fuming colorless liquid with an ammonia-like odor.

II. HEALTH HAZARD DATA

A. Ways in Which the Chemical Affects Your Body: Monomethyl hydrazine can affect your body if you inhale it, if it comes in contact with your eyes or skin, or if you swallow it. It may enter your body through your skin.

B. Effects of Overexposure:

1. Short-Term Exposure: Monomethyl hydrazine may cause irritation of the eyes and respiratory tract. It may

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also cause nausea, diarrhea, and convulsions. Exposure to this chemical may reduce the ability of the blood to carry oxygen. The exposed person may have a bluish color. Breakdown of the red blood cells, anemia and kidney damage may also occur. Exposure to the liquid may cause eye and skin irritation.

2. Long-Term Exposure: None known.
3. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms and suspect they are caused by exposure to monomethyl hydrazine.

III. EMERGENCY FIRST AID PROCEDURES

- A. Eye Exposure: If monomethyl hydrazine gets into your eyes, wash the eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
- B. Skin Exposure: If monomethyl hydrazine gets on your skin, immediately flush skin with water. If monomethyl hydrazine soaks through your clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.
- C. Breathing: If you or any other person breathes in large amounts of monomethyl hydrazine 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.
- D. Swallowing: When monomethyl hydrazine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
- E. Rescue: Move 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 yourself. Understand your emergency rescue procedures and know the locations of the equipment before the need arises.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

- A. Respirators: Respirators are not the best way to control exposure to monomethyl hydrazine. You can only be required to wear them for routine use if your employer is in the process of installing controls or control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration (MESA) or National Institute for Occupational Safety and Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.) For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work

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situations where there use is required. If you can smell monomethyl hydrazine while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.

- B. Supplied-air suits: in some work situations the wearing of supplied-air suits may be necessary. Your employer should instruct you in their proper use and operation.
- C. Protective Clothing: You must wear impervious clothing, gloves, face shield or other appropriate protective clothing to prevent any possibility of skin contact with liquid monomethyl hydrazine. Replace or repair impervious clothing that has developed leaks.
- D. Eye Protection: You must wear splash-proof safety goggles where there is any possibility of liquid monomethyl hydrazine contacting your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

- A. Monomethyl hydrazine is a flammable liquid and its vapors can easily form explosive mixtures in air over a wide range. It may ignite spontaneously when in contact with porous materials such as earth, asbestos, wood or cloth.
- B. Monomethyl hydrazine must be stored in tightly closed containers in a cool, well ventilated area away from heat, sparks, flames, oxidizers (such as hydrogen peroxide and nitric acid), oxides of iron and copper, manganese, lead and copper and its alloys. Anhydrous monomethylhydrazine must be stored under a nitrogen atmosphere.
- C. Sources of ignition such as smoking and open flames are prohibited wherever monomethyl hydrazine is handled, used or stored.
- D. You must use non-sparking tools when opening or closing metal containers of monomethyl hydrazine, and containers must be bonded and grounded when pouring or transferring liquid monomethyl hydrazine.
- E. You must immediately remove any non-impervious clothing that becomes contaminated with monomethyl hydrazine and this clothing must not be reworn until the monomethyl hydrazine is removed from the clothing.
- F. Clothing wet with liquid monomethyl hydrazine can be easily ignited. You must immediately remove this clothing and it must not be reworn until the monomethyl hydrazine is removed from the clothing.
- G. If your skin becomes contaminated with monomethyl hydrazine, you must immediately wash or shower to remove the monomethyl hydrazine from your skin.
- H. You must not eat or smoke in areas where liquid monomethyl hydrazine is handled, processed or stored.
- I. If you handle liquid monomethyl hydrazine, you must wash your hands thoroughly with water before eating, smoking or using toilet facilities.
- J. Fire extinguishers, eye flushing facilities and quick drenching facilities, where provided, must be readily

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available and you should know where they are and how to operate them.

- K. Ask your supervisor where monomethyl hydrazine is used in your work area and for any additional plant safety and health rules.

VI. ACCESS TO INFORMATION

- A. Each year your employer is required to inform you of the information contained in this Substance Safety Data Sheet for monomethyl hydrazine. In addition, your employer must instruct you in the safe use of monomethyl hydrazine, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to monomethyl hydrazine. You or your representative have the right to observe employee exposure measurements and to record the results obtained. If your employer determines that you are being overexposed, he is required to inform you of the exposure and of the actions which are being taken to reduce your exposure.
- C. Your employer is required to keep records of exposure determinations, exposure measurements, and medical surveillance. Your employer is required to make records of exposure determinations and your exposure measurements available to you or your representative upon your request. Your employer is required to release your medical records to your physician upon your written request.

APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
FOR MONOMETHYL HYDRAZINE

I. PHYSICAL AND CHEMICAL DATA

- A. Substance Identification
1. Synonyms: Methyl hydrazine
 2. Formula: CH3NHNH2
 3. Molecular weight: 46.1
- B. Physical Data
1. Boiling point (760 mm Hg): 87.5 C (190 F)
 2. Specific gravity (water = 1): 0.88
 3. Vapor density (air = 1 at boiling point of monomethyl hydrazine): 1.6
 4. Melting point: -52 C (-62 F)
 5. Vapor pressure at 20 C (68 F): 37.5 mm Hg
 6. Solubility in water, % by weight at 20 C (68 F): Soluble in proportions.
 7. Evaporation rate (butyl acetate = 1): Data not available

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8. Appearance and odor: Fuming colorless liquid with an ammonia-like odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: -8.9 C (17 F) (closed cup)
2. Autoignition temperature: 194 C (382 F)
3. Flammable limits in air, % by volume: Lower: 2.5; Upper: 98
4. Extinguishing media: Carbon dioxide or dry chemical for small fires; because of the wide flammable limits, low flash point, and reignition hazard of monomethyl hydrazine, water dilution may be more effective than dry chemical or carbon dioxide.
5. Special fire-fighting procedures: Do not use a solid stream of water since the stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Monomethyl hydrazine is a flammable liquid. Its vapors can easily form explosive mixtures with air over a wide range. All ignition sources must be controlled where monomethyl hydrazine is handled, used or stored. Monomethyl hydrazine vapors are heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which monomethyl hydrazine is handled.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, monomethyl hydrazine is classified as a Class IB flammable liquid. For example, above 6300 ppm, approximately one-fourth of the lower flammable limit, is one situation in which monomethyl hydrazine is considered to be a potential fire and explosion hazard.
8. For purposes of complying with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electrical Code for monomethyl hydrazine shall be Class I Group C.

B. Reactivity

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Monomethyl hydrazine is a highly reactive reducing agent and contact with oxides of iron or copper, and contact with manganese, lead or copper and its alloys can lead to fires and explosions. Monomethyl hydrazine when spread on a large surface may ignite spontaneously. It may ignite spontaneously in air when in contact with porous materials such as earth, asbestos, wood or cloth, or with oxidants like hydrogen peroxide or nitric acid.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving monomethyl hydrazine.

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

III. SPILL, LEAK, AND DISPOSAL PROCEDURES

- A. 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. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for vapors to completely clear hood ductwork, then burn the paper. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Monomethyl hydrazine may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
 4. For larger quantities, dilute with water, flush to a safe area and neutralize with hydrochloric or sulfuric acid.
- B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until cleanup has been completed.
- C. Waste disposal methods: Monomethyl hydrazine may be disposed of:
 1. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
 2. By holding diluted material in a suitable pond and destroying with hydrogen peroxide or high-test hypochlorite (HTH).

IV. MONITORING AND MEASUREMENT PROCEDURES

- A. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken during periods of maximum expected airborne concentrations of monomethyl hydrazine. Each measurement should consist of a 15-minute sample or series of consecutive samples totaling fifteen (15) 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 a good estimate of the employee's highest exposure for that shift. Sampling and analyses may be performed by calibrated instruments such as detector tubes certified by NIOSH under 42 CFR part 84, portable direct-reading instruments, dosimeters, or gas and vapor adsorption tubes with subsequent chemical analyses. The method of measurement must determine the concentration of monomethyl hydrazine to plus or minus 35%.
- B. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring and measurements under this section should be essentially the same as described above. More than three (3) measurements should be taken during the work shift so that increased confidence may be placed in the judgement that the employee

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has or has not, in fact, been exposed in excess of the permissible limit. Samples should be collected as described in paragraph IV. a. Laboratories performing chemical analyses should be accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association. The method of measurement must determine the concentration of monomethyl hydrazine to plus or minus 25%.

- C. METHODS: Methods meeting these accuracy requirements are available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161 under the title "NIOSH Analytical Methods for Set K" (Order number XXXXXXXXXXXX).
- D. QUALIFIED PERSONS: Since many of the duties relating to employee protection are dependent on the results of monitoring and measuring procedures, employers should assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.

V. MISCELLANEOUS PRECAUTIONS

- A. Store monomethyl hydrazine under nitrogen gas in tightly closed containers in a cool, well ventilated area.
- B. High exposures to monomethyl hydrazine can occur when transferring the liquid from one container to another.
- C. Non-sparking tools must be used to open and close metal monomethyl hydrazine containers. These containers must be effectively grounded and bonded prior to pouring.
- D. Use of supplied-air suits or other impervious coverings may be necessary to prevent skin contact with monomethyl hydrazine where the concentration of monomethyl hydrazine is unknown or is greater than 5 ppm. Supplied-air suits should be selected, used, and maintained under the immediate supervision of persons knowledgeable in the limitations and potential life endangering characteristics of supplied-air suits.
- E. Employers should advise employees of all areas and operations where exposure to monomethyl hydrazine could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to monomethyl hydrazine is likely to occur are: during its production and its use as a component of rocket propellant fuels, and its use in the synthesis of pharmaceuticals, pesticides and in polymer technology.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

— Inhalation; skin absorption.

II. TOXICOLOGY

Monomethyl hydrazine vapor is a convulsant and a respiratory irritant. Exposure of dogs to 29 ppm and to 21 ppm, both for 4 hours, resulted in

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respiratory irritation, convulsions, and some deaths; postmortem examination revealed no lesions attributable primarily to monomethyl hydrazine although secondary manifestations probably due to convulsions included pulmonary hemorrhage and edema; toxic signs also occurred at 15 ppm. In dogs which survived exposure there was evidence of moderately severe intravascular hemolysis. In another study additional signs were noted in dogs including eye irritation, tremors, ataxia, diarrhea, and cyanosis. Monomethyl hydrazine produced methemoglobin in vitro in human blood and in the blood of some animal species. The liquid is irritating to the skin. Continuous exposures for 90 days to this substance at 0.5 ppm resulted in severe toxic effects and possibly some mortality in monkeys, rats and mice. This may be interpreted to indicate a rather small factor of safety in the threshold limit value for this substance. This is considered to be an extremely toxic substance. Carcinogenic effects have been reported in animals.

III. SIGNS AND SYMPTOMS

May cause eye irritation, vomiting and diarrhea, respiratory irritation, tremors and ataxia; may produce signs of anoxia including cyanosis; may also cause convulsions.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Immediately flush eyes and skin with water. If swallowed and the person is conscious, induce vomiting. Give artificial resuscitation if indicated. Recovery is usually rapid and complete. Observe for convulsions and institute appropriate treatment.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

In animals, monomethyl hydrazine is a respiratory irritant and convulsant. Skin absorption is known to occur. It is important that the physician become familiar with plant operating conditions in which exposure to monomethyl hydrazine occurs. Those with skin disease may not tolerate the wearing of protective clothing and those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

B. PREPLACEMENT

The following medical procedures must be made available to each employee who is exposed to monomethyl hydrazine:

1. A complete history and physical examination -- The purpose is to detect preexisting conditions that might place the exposed

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employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver, blood, respiratory system, cardiovascular system, and eyes should be stressed.

2. Liver function tests -- Monomethyl hydrazine may cause liver damage. A profile of liver function shall be obtained using a medically acceptable array of biochemical tests.
3. Complete blood count -- This compound has been shown to cause hemolysis and anemia. A complete blood count must be performed to include red and white cell count, a differential count of a stained blood smear, as well as hemoglobin and hematocrit.
4. 14" x 17" chest roentgenogram -- Monomethyl hydrazine may cause lung damage. Surveillance of the lungs is indicated.
5. FVC and FEV (1 sec) -- Monomethyl hydrazine may cause lung damage. Periodic surveillance is indicated.

C. PERIODIC EXAMINATIONS

The above medical examinations are to be repeated on an annual basis except that an X-ray is required only when indicated by pulmonary function testing.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienists: "Monomethylhydrazine," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 174-175.
2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 2218-2222.
3. Jacobson, K.H., et al: "The Acute Toxicity of the Vapors of Some Methylated Hydrazine Derivatives," AMA Archives of Industrial Health, 12:609-616, 1955.
4. Haun, C.C., et al: "Acute Inhalation Toxicity of Monomethylhydrazine Vapor," American Industrial Hygiene Association Journal, 31:667-677, 1970.
5. Clark, D.A. and S.R. Fortney: "Methemoglobinemia as an Indicator of Exposure to Monomethylhydrazine," Aerospace Medicine, 38:1230-1234, 1967.
6. Toth, B. and Shimizu, H.: "Methylhydrazine Tumorigenesis in Syrian Golden Hamsters and the Morphology of Malignant Histiocytomas," Cancer Research, 33:2744-2749, 1973.

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7. Grant, W. Morton: Toxicology of the Eye, (2d ed.), Charles C. Thomas, Illinois, 1974, p.694.

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REFERENCES AND SOURCES
MONOMETHYL HYDRAZINE

1910.93

- (d) Compliance - Open surface tanks classification based on boiling point and guidelines in ANSI Z9.1.
- (e) Fire and Safety
 - (1) Electrical - Classification based on "Fire Hazard Classification of Chemical Vapors Relative to Explosion-proof Electrical Equipment," H. Carhart et al, National Academy of Sciences, 1973, report to U. S. Coast Guard, report no. CG-D-92-74, p. 17.
- (f) Personal Protective Equipment, and, (h) Sanitation
 - Eyes: Grant, "Toxicology of the Eye;" "Encyclopedia of Occupational Safety and Health," International Labour Organization
 - Skin: "Monomethyl Hydrazine," Olin Chemical Co.; Patty, "Industrial Hygiene and Toxicology;" Grant, "Toxicology of the Eye"
 - Ingestion: Patty, "Industrial Hygiene and Toxicology;" "Encyclopedia of Occupational Safety and Health," International Labour Organization; "Documentation of Threshold Limit Values"

COMMENTS

Eye - Classification: 1

Output statement numbers: 9, 13

Exceptions: None

Grant notes "monomethyl hydrazine (MMH) to be peculiarly toxic to the cornea . . . (and) in excised corneas, solutions as dilute as 10 to the negative seventh molar promote swelling of the cornea." The ILO reports "MMH can cause permanent corneal lesions." A classification of 1 is clearly warranted.

Skin - Classification: 1

Output statement numbers: 1, 7a, 8a, 14g and 21 combined, 14i

Exceptions: None

The Olin Chemical Co. states that "monomethyl hydrazine is only temporarily irritating in skin tests, causing local damage resembling burns." According to Patty, MMH is "less active than hydrazine, causing a sensitization type dermatitis." A guinea pig LD50 of 56 cu mm/kg is listed. This is equivalent to 0.056 ml/kg. Grant notes "when applied to the skin of dogs, (MMH) is absorbed and carried by the bloodstream to the eyes where it enters the aqueous humor readily and is injurious to the endothelium of the cornea, causing corneal edema in 5 to 6 hours." The vapor pressure of the substance is 37.5 mm Hg at 20 C. It is miscible in all proportions with water and has a flashpoint of 63 F.

The extremely low skin penetration LD50 reported and observed effects of exposure, as noted above and in the following, lead to the conclusion that a classification of 1 is justified. Statement 6, however, is considered too stringent and is replaced by 7a.

Ingestion - Classification: 1

Output statement numbers: 19, 20a

Exceptions: None

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Patty reports that intoxication by monomethyl hydrazine, "most toxic of the methyl derivatives (of hydrazine), causes central nervous system stimulation with terminal convulsions." He continues, "MMH hemolyzes red blood cells, resulting in blood cell destruction and anemia." The ILO lists methaemoglobinemia, kidney damage, convulsions and nausea as the most prominent effects of overexposure. Witkins gives an oral mouse LD50 of 33 plus or minus 6 mg/kg and an oral rat LD50 of 32.5 plus or minus 1.4 mg/kg. The Documentation of T reports "that while a single injection of 10 mg/kg was tolerated by monkeys, doses of 5 mg/kg repeated daily caused emesis and convulsions when a total dose of 15 mg/kg was reached." They add "all animals tolerated 2.5 mg/kg daily for 23 days." The extreme toxicity of the substance indicates that a classification of 1 is warranted.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1973 (NFPA)

Olin Chemicals, "Monomethyl Hydrazine, Handling and Storage" (Olin)

Kirk-Othmer, "Encyclopedia of Chemical Technology" 2nd edition, Vol. 11, p. 169 (K-O)

Sources of data items used:

- I. A. 1. Synonyms: K-O
- 2. Formula: NFPA-325M; Olin
- 3. Molecular weight: Olin
- B. 1. Boiling point: NFPA-325M; Olin
- 2. Specific gravity: Olin
- 3. Vapor density: NFPA-325M; Olin
- 4. Melting point: Olin
- 5. Vapor pressure: Olin
- 6. Solubility in water: Olin
- 7. Evaporation rate: Data not available
- 8. Appearance and odor: Olin; K-O
- II. A. 1. Flash point: NFPA 49
- 2. Autoignition temperature: Olin
- 3. Flammable limits: Olin
- 4. Extinguishing media: NFPA-325M; Olin
- 5. Special fire fighting procedures: Olin; ADL
- 6. Unusual fire and explosion hazards: ADL
- B. 1. Conditions contributing to instability: ADL, NFPA 491M
- 2. Incompatibilities: Olin, NFPA 49
- 3. Hazardous decomposition products: ADL
- 4. Special precautions: ADL
- III. A. Steps if released or spilled: Olin: ADL
- C. Waste disposal method: Olin
- V. Miscellaneous precautions: Olin

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

Byrkit, G. D., and Muchalek, G. A., "Hydrazine in Organic Chemistry," Ind. Eng. Chem, 42, 1862-75 (1950) (Byrkit)

Chemical Abstracts, 66-75 (1967-71); 80 (1974), Chemical Abstracts Service

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(CA)

Grant, W. M., "Toxicology of the Eye," 2nd ed., Thomas, C. C., 1974 (Grant)
Hawley, G. G., "The Condensed Chemical Dictionary," 8th ed., Van Nostrand-Reinhold, 1971 (Hawley)
International Labour Organization, "Encyclopedia of Occupational Health and Safety," Geneva, 1972 (ILO)
Kirk, R., Othmer, D. "Encyclopedia of Chemical Technology," Interscience, 1st ed, 1954 (Chem Tech); 2nd ed., 1972 (K-0)
Monomethyl Hydrazine: Liquid Propellant Information Agency, "Liquid Propellant Manual," December 1961 (Propellants)
Olin Chemicals, "Monomethyl Hydrazine Handling and Storage," (Olin)
Patty, F. A., "Industrial Hygiene and Toxicology," Vol. II, Interscience, 1962 (Patty)
Stanford Research Institute, "Chemical Economics Handbook," Menlo Park, California (SRI)

References for Specific Use/Exposure

1. Olin, ILO, K-0, CA, Propellants
2. CA, Hawley
3. CA, Hawley
4. ILO, Chem Tech, K-0, Propellants, SRI
5. CA
6. Byrkit, CA, Hawley
7. CA

References for Specific Control Methods

ILO, Olin, Propellants, Patty, Grant, CA

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Monomethyl Hydrazine

D. O. L. STANDARD: 0.2 ppm

WARNING PROPERTIES:

Odor Threshold: According to the Documentation of TLV's, the odor threshold of monomethyl hydrazine has been reported to be 1 to 3 ppm.

Eye Irritation Level: No quantitative information is available concerning the concentrations of monomethyl hydrazine which produce eye irritation. The Product Data Sheet of Olin Chemicals, however, reports that "continuous exposure of the eye to vapors will cause eye irritation and conjunctivitis."

Other Information: The Product Data Sheet of Olin Chemicals also reports that "inhalation of the vapor can cause irritation of the respiratory tract," but no quantitative information is given.

Evaluation of Warning Properties: Monomethyl hydrazine has poor warning properties. The odor threshold is many times greater than the permissible exposure limit, and no quantitative information is available relating the irritant effects of monomethyl hydrazine and air concentrations. Gas sorbent respiratory equipment is not permitted.

IDLH: 5 ppm

Basis for IDLH Value: This IDLH is based upon Jacobson's report of an LC50 of 5.6 ppm for mice for monomethyl hydrazine.

Other Toxicological Information: The Documentation of TLV's states that monomethyl hydrazine (MMH) is "the strongest convulsant and

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the most toxic of the methyl derivatives. MMH exposures produced greater severity of muscular contractions and respiratory distress and moderately severe intravascular hemolysis - a response not seen with other related hydrazines." The ILO notes that "monomethyl hydrazine is a strong methemoglobin former."

Jacobson et al. observed mortality in 2 out of 3 dogs exposed to 21 ppm monomethyl hydrazine for 4 hours. Jacobson also reported the following 4-hour LC50 values: 74 ppm for rats; 5.6 ppm for mice; and 143 ppm for hamsters.

The Documentation of TLV's reports the following LC50 values: for a 60-minute exposure, 82 ppm for squirrel monkeys and 244 ppm for rats; for a 240-minute exposure, 78 ppm for rats.

Patty reports a skin penetration LD50 for the guinea pig of 56 mm³/kg.

LFL: 25,000 ppm

VAPOR PRESSURE: 37.5 mm Hg at 20 deg. C.

SATURATED CONCENTRATION AT 20 DEG. C.: 49,300 ppm

Reference: Jacobson, K. H., Clem, J. H., Wheelwright, H. J., Rinehart, W. E. and Mayes, N., AMA Archives of Ind. Health, 12:609, 1955.

NOTE: Since all organic vapor cartridges may not be efficient in removing monomethyl hydrazine only those cartridges and canisters which provide protection against monomethyl hydrazine are permitted.

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	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of mist and skin contact with liquid or mist during use in preparation and handling of liquid rocket propellants (used as a high energy rocket fuel)	A,B,D	Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice
2.	Inhalation of mist and skin contact with liquid or mist during use as a chemical intermediate for synthesis of pharmaceuticals (antiinflammatories, analgesics, antihypertensives, antidepressants)	A,B,D	Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice
3.	Inhalation of mist and skin contact with liquid or mist during use as a chemical intermediate for the synthesis of pesticides (anthelminics, insecticides, acaricides)	A,B,D	Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice
4.	Inhalation of mist and skin contact with liquid or mist during manufacture and distribution of monomethyl hydrazine and during maintenance of storage containers	A,B,D	Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice
5.	Inhalation of mist and skin contact with liquid or mist during use in polymer technology (as copolymer, catalyst, initiator, decolorizing agent)	A,B,D	Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice
6.	Inhalation of mist and skin contact with liquid or mist during use for general organic synthesis	A,B,D	Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice

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| 7. | Inhalation of mist and skin contact with liquid or mist during miscellaneous uses (in electroplating baths, etching solutions, photographic processing) | A,B,D | Local exhaust ventilation; personal protective equipment (gloves, goggles, face shield, protective clothing, respiratory protective devices); good personal hygiene practice |
|----|---|-------|--|

- A -- Inhalation
- B -- Skin and eye contact resulting in Localized irritation
- C -- Ingestion
- D -- Skin contact resulting in absorption and subsequent systemic poisoning