

Safety Data Sheet

Methylhydrazine

Division of Safety
National Institutes
of Health



WARNING!

THIS COMPOUND IS ABSORBED THROUGH THE SKIN AND THE RESPIRATORY AND INTESTINAL TRACTS. IT IS TOXIC, CARCINOGENIC, MUTAGENIC, AND TERATOGENIC. IT IS FLAMMABLE AND EXPLOSIVE AND MAY IRRITATE TISSUES. AVOID FORMATION AND BREATHING OF AEROSOLS AND VAPORS.

LABORATORY OPERATIONS SHOULD BE CONDUCTED IN A FUME HOOD, GLOVE BOX, OR VENTILATED CABINET.

AVOID SKIN CONTACT: IF EXPOSED, WASH WITH SOAP AND WATER.

FOR EYE EXPOSURE, IRRIGATE IMMEDIATELY WITH LARGE AMOUNTS OF WATER. FOR INGESTION, DRINK PLENTY OF MILK OR WATER. INDUCE VOMITING. FOR INHALATION, REMOVE VICTIM PROMPTLY TO CLEAN AIR. ADMINISTER RESCUE BREATHING IF NECESSARY. REFER TO PHYSICIAN.

IN CASE OF LABORATORY SPILL, WEAR PROTECTIVE CLOTHING DURING CLEANUP. AVOID SKIN CONTACT OR BREATHING OF AEROSOLS OR VAPORS. USE WATER TO DISSOLVE COMPOUND. WASH DOWN AREA WITH SOAP AND WATER. DISPOSE OF WASTE SOLUTIONS AND MATERIALS APPROPRIATELY.

A. Background

Methylhydrazine (MHZ) is a colorless, volatile, hygroscopic liquid with an ammonia-like odor; it is flammable and is easily oxidized by atmospheric oxygen. MHZ is a strong irritant to the eyes and respiratory tract; toxic in laboratory animals; and a carcinogen, mutagen, and teratogen in several species. It has been evaluated as a rocket fuel and used as a solvent and chemical intermediate.

B. Chemical and Physical Data

1. Chemical Abstract No.: 60-34-4

issued 8/82

2. Synonyms:

MHZ	1-Methylhydrazine	Methylhydrazine
Hydrazomethane	Monomethylhydrazine	

3. Molecular formula: CH_6N_2 structure: $\text{NH}_2\text{-NH-CH}_3$

weight:
46.07

4. Density: 0.874 g/cm³.

5. Absorption spectroscopy: IR, Raman, and NMR spectra are listed by Grasselli and Ritchey (1975).

6. Volatility: Vapor pressure = 49.6 mm Hg at 25°C.

7. Solubility: Miscible with water, ethanol; soluble in ether.

8. Description, appearance, and odor: Colorless, volatile, hygroscopic liquid with ammonia-like odor.

9. Boiling point: 87.5°C.

Melting point: Listed as -52.4°C (Windholz, 1976) and less than -80°C (Weast, 1979).

10. Stability: Explosive at high temperatures; slowly oxidized on exposure to air.

11. Chemical reactivity: MHZ is a strong base and forms salts with mineral acids. As a strong reducing agent, MHZ is oxidized by compounds such as peroxides, iodates, ferricyanide, and ceric ions in acid solution.

12. Flash point: 21.1°C, Cleveland open cup.

13. Autoignition temperature: 196°C (Bretherick, 1975).

14. Flammable limits in air: 2.5 - 97±2% (Windholz, 1976).

Fire, Explosion, and Reactivity Hazard Data

1. Use large amounts of water to extinguish fires and to minimize reignition and flashback hazard. Fire-fighting personnel should wear air-supplied respirators with full-face masks.

2. MHZ is highly flammable and its vapors in air can produce explosive mixtures.

3. Conditions contributing to instability include exposure to atmospheric oxygen, heat, and ultraviolet light.
4. Incompatible with oxidizing agents and metallic oxides.
5. Incomplete oxidation may result in hazardous decomposition products (hydrogen, ammonia, methylamine, hydrazoic acid).
6. Do not expose to sparks or open flames. Use nonspark tools. Store in an explosion-safe refrigerator only.

Operational Procedures

The NIH Guidelines for the Laboratory Use of Chemical Carcinogens describe operational practices to be followed when potentially carcinogenic chemicals are used in NIH laboratories. The Guidelines should be consulted to identify the proper use conditions required and specific controls to be implemented during normal and complex operations or manipulations involving MHZ.

HZ penetrates various glove materials (Luskus et al., 1980). This factor should be taken into account when handling MHZ.

1. Chemical inactivation: No validated method reported.
2. Decontamination: Turn off equipment that could be affected by MHZ or the materials used for cleanup. If more than 10 ml has been spilled or if there is any uncertainty regarding the procedures to be followed for decontamination, call the NIH Fire Department (dial 116) for assistance. Wash surfaces with copious quantities of water. Glassware should be rinsed (in a hood) with water and washed with soap and water. Animal cages should be washed with water.
3. Disposal: No waste streams containing MHZ shall be disposed of in sinks or general refuse. Surplus MHZ or chemical waste streams contaminated with MHZ shall be handled as hazardous chemical waste and disposed of in accordance with the NIH chemical waste disposal system. Nonchemical waste (e.g., animal carcasses and bedding) containing MHZ shall be handled and packaged for incineration in accordance with the NIH medical-pathological waste disposal system. Potentially infectious waste (e.g., tissue cultures) containing MHZ shall be packaged for incineration, as above. Burnable waste (e.g., absorbent bench top liners) minimally contaminated with MHZ shall be handled as potentially infectious waste and packaged for incineration, as above. Absorbent materials (e.g., associated with spill cleanup) grossly contaminated shall be handled in accordance with the chemical waste disposal system. Radioactive waste containing MHZ shall be handled in accordance with the NIH radioactive waste disposal system.

4. Storage: Store in sealed ampoules, in bottles with caps having polyethylene cone liners, or in screw-capped vials with Teflon liners in an explosion-safe refrigerator. For long-term storage, a freezer is preferred; however, stocks must be protected against moisture and brought to room temperature prior to sampling to avoid introducing moisture.

Monitoring and Measurement Procedures Including Direct Field Measurements and Sampling for Subsequent Laboratory Analysis

1. Sampling: For quantitative measurements of air samples, glass bubblers charged with hydrochloric acid are used. For monitoring purposes, sampling and detection tubes, a personnel monitor (based on reduction of a metal salt and completing an electric circuit), and a dosimeter (colorimetric reaction, Plantz et al., 1968) have been developed; some of these items are commercially available. No special procedures have been developed for water sampling. Weeks et al. (1976) describe a method whereby surface samples are taken with filter paper, which is then moistened with ethanol followed by addition of fluorescence-producing agent.
2. Separation and analysis: Methods developed up to 1970 have been reviewed (Malone, 1970). Colorimetry, involving reaction with p-dimethylaminobenzaldehyde (Ehrlich's reagent), has been applied to determination of MHZ in serum (minimal detectable level, 0.5 $\mu\text{g/ml}$) and in bubbler solutions from air sampling. The reduction of phosphomolybdic acid to form a blue complex has been used (minimal detectable level, 35 $\mu\text{g/m}^3$ from a 20-liter air sample), but this method is subject to interference by other reducing agents, including hydrazine and other methylated hydrazines. Greater specificity and/or sensitivity has been achieved by using TLC with the Folin-Ciocalteu reagent (Fiala and Weisburger, 1975). A fairly specific GC procedure in which MHZ is converted to a pyrazole derivative has been applied to aqueous solutions (Dee, 1971).

Biological Effects (Animal and Human)

1. Absorption: MHZ is readily absorbed through the respiratory and intestinal tracts and through the intact skin. Eye exposure causes severe irritation.
2. Distribution: No data. Since MHZ on long-term exposure produces effects in the liver, kidneys, and blood, one may assume that these organs are distribution targets of MHZ or a metabolite.
3. Metabolism and excretion: Metabolites of MHZ have been identified only in in vitro enzymatic systems and include methane, formaldehyde, and N-oxidized intermediates (Prough, 1973). The latter, having structures similar to known carcinogens, may be the reason for carcinogenic action of MHZ. MHZ is excreted via lungs and kidneys; the clearance mechanism depends on species and dose (Pinkerton et al., 1967).

4. Toxic effects: The oral LD50s in the hamster, mouse, and rat are 22, 33, and 71 mg/kg, respectively, and the skin LD50s in the hamster and rat are 239 and 183 mg/kg, respectively. Inhalation LC50s are 56 and 74 ppm in 240 minutes in mice and rats, respectively, and 82 and 96 ppm in 60 minutes in monkeys and dogs, respectively. Acute toxic effects following inhalation of MHZ in several species are irritation of eyes, nose, and throat; emesis; ataxia; and convulsions. A major toxic effect on chronic exposure is methemoglobinemia and tonic-clonic seizures (in monkeys and cats), suggesting that the central nervous system is also a target organ.
5. Carcinogenic effects: These are species dependent; oral administration of MHZ to hamsters produces liver and cecum tumors, while in the mouse, only lung tumors are found.
6. Mutagenic and teratogenic effects: MHZ is active in the Ames test and causes chromosome breaks. Teratogenicity has been noted in toads, mice, and rabbits.

G. Emergency Treatment

1. Skin and eye exposure: For skin exposure, remove contaminated clothing and wash skin with soap and water. Avoid raising skin temperature. For eye exposure, irrigate immediately with copious quantities of running water for at least 15 minutes.
2. Ingestion: Drink plenty of milk or water. Induce vomiting.
3. Inhalation: Remove victim promptly to clean air. Administer rescue breathing if necessary.
4. Refer to physician. Ophthalmological consultation and treatment for laryngeal and pulmonary irritation and edema may be required.

H. References

- Bretherick, L., ed. 1975. Handbook of Reactive Chemical Hazards. CRC Press, Cleveland, OH.
- Dee, L.A. 1971. Gas chromatographic determinations of aqueous trace hydrazine and methyl hydrazine as corresponding pyrazoles. Anal Chem 43:1416-1419.
- Fiala, E.S., and J.H. Weisburger. 1975. Thin-layer chromatography of some methylated hydrazines and detection by a sensitive spray reagent. J Chromatogr 105:189-192.
- Grasselli, J.G., and W.M. Ritchey, eds. 1975. Atlas of Spectral Data and Physical Constants for Organic Compounds, 2nd ed. CRC Press, Cleveland, OH.
- Luskus, L.J., H.J. Kilian, J.W. Mokry, M.L. Turpin. 1980. Test and Evaluation for Chemical Resistance of Gloves Worn for Protection Against Exposure to H-70 Hydrazine. Report SAM-TR-80-15. USAF School of Aerospace Medicine, Brooks Air Force Base, TX.

1970. The Determination of Hydrazine-Hydrazide Groups. Pergamon Press, Elmsford, New York.
- Pinkerton, M.K., E.A. Hagan, and K.C. Back. 1967. Distribution and excretion of monomethylhydrazine- ^{14}C . US NTIS No. AD-666662. 24 pp.
- Plantz, C.A., P.W. McConnaughey, and C.C. Jenca. 1968. Colorimetric personal dosimeter for hydrazine fuel handlers. Am Ind Hyg Assoc J 29:162-164.
- Prough, R. 1973. The N-oxidation of alkylhydrazines catalyzed by the microsomal mixed-function amine oxidase. Arch Biochem Biophys 158:442-444.
- Weast, R.C., ed. 1979. Handbook of Chemistry and Physics, 60th ed. CRC Press, Cleveland, OH.
- Weeks, R.W., Jr., S.K. Yasuda, and B.J. Dean. 1976. Fluorescent detection of hydrazines via fluoescamine and isomeric phthalaldehydes. Anal Chem 48:159-161.
- Windholz, M., ed. 1976. Merck Index, 9th ed. Merck and Co., Inc. Rahway, NJ.