TETRAMETHYLAMMONIUM HYDROXIDE GUIDELINES

Tetramethylammonium hydroxide (TMAH) is a quaternary ammonium salt with the molecular formula $(CH_3)_4NOH$. It is widely used in micro- or nanofabrication as an etchant and developer. TMAH is typically one of several ingredients in commercial etching / stripping mixtures, although it may also be used as a pure chemical. It is strongly basic and is known to be highly toxic if ingested or skin contact occurs. Anyone who works in laboratories containing TMAH should familiarize themselves with its SDS and a clear Standard Operating Procedure (SOP) should be established. Therefore, careful precautions should always be taken when handling this chemical. This document discusses the properties, health and safety hazards, how to properly handle and store TMAH. Also included are emergency procedures for dealing with accidental TMAH contact, including first aid treatment information.

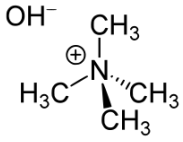
☠WARNING☠: In addition of being a highly corrosive liquid, TMAH is toxic and may be fatal if swallowed. It is harmful if inhaled or absorbed through skin. It can causes burns to any area of contact. The liquid can produce toxic and corrosive vapors which are harmful and may cause blindness.

1. Properties

Names: tetramethylammonium hydroxide; N,N,N,-trimethylmethanaminium hydroxide; tetramethylazanium hydroxide; TMAH; TMAOH.

Chemical Formula: $(CH_3)_4NOH$

Chemical Structure:



CAS #: 75-59-2

Physical aspect: Sold either as solid tetramethylammonium hydroxide pentahydrate or as 10-40 wt% solutions in water or methanol.

Solution 25 wt% in water: Colorless to straw-colored liquid
Strong ammonia-like odor (smells like dead fish if it is not pure, from trimethylamine impurity) – *TMAH has virtually no odor when pure*
100% soluble in water.

Physical and toxicological properties of TMAH are summarized in **Table 1**.

Table 1. Physical and Toxicological Properties of TMAH (25 wt% in water)

Molar Mass	91.15 g mol^{-1}
Boiling point	102°C
Flash point	>93°C
Vapor pressure	17.5 mm Hg at 20°C
Density	1.02g·cm^{-3}
pH	>13
PEL (TWA)	N/A
IDHL	N/A

2. Hazard Classification (TMAH 25% wt% in water)

WHMIS (2015):

Acute toxicity, Oral (Category 2)
Acute toxicity, Dermal (Category 2)
Skin corrosion/irritation (Category 1)
Serious eye damage/eye irritation (Category 1)
Specific target organ toxicity - single exposure (Category 1), Central nervous system
Specific target organ toxicity - repeated exposure, Dermal (Category 1), thymus gland, Liver

NFPA 704:

Flammability: Non-flammable or combustible (water solutions)
Health hazard: Potential of severe acute effects: highly toxic by ingestion, toxic by skin absorption.
Instability/Reactivity: Stable; not known to polymerize. Reacts vigorously with strong acids and oxidizers.

3. Reactivity, Fire and Explosion Hazards

TMAH solution is stable under ordinary conditions of use and storage. It readily absorbs CO_2 from the air. Solutions in water are not flammable or combustible. However, solutions in methanol will be flammable. TMAH solutions will be volatilized and consumed in general fire and the vapors and fumes are corrosive and may also be toxic (oxides of nitrogen). Heat, flames, and ignition sources should be avoided. Regular water spray, alcohol-resistant foam, dry chemical or carbon dioxide extinguishers are suitable extinguishing media.

TMAH will not decompose to different carbon oxides, nitrogen oxides and formaldehyde gas when heated to decomposition. Hazardous polymerization will not occur. TMAH is incompatibilities with strong acids and oxidizing agents. It will attack many plastics and rubber. It may react with metallic aluminum and generate hydrogen gas, which is flammable.

4. Health Hazards

Exposure to TMAH will result in acute health effects such as intense burning of the eyes, nose, throat, lungs and skin. Solution, mist and spray are very corrosive to skin, eyes and mucous membranes and may cause dermatitis or permanent eye damage. If ingested, burns to the oesophagus and stomach will occur with potential risk of perforation. TMAH has not been tested for cancer, reproductive or any other long-term chronic effects. Experimental studies have indicated that TMAH is a weak inhibitor of acetylcholinesterase and acts as a cholinergic (muscarinic and nicotinic) agonist. Depending on exposure's level and duration, signs and symptoms may include blurred or double vision, pinpoint pupils, changes in heart rate and blood pressure, abdominal cramping, nausea and vomiting, diarrhea, sweating or bronchial secretions, urinary incontinence, muscle twitching, tremors or convulsions. Other symptoms consistent with cholinergic activity may also be observed.

While it has long been known to be very toxic if ingested, industrial experience indicates that skin exposure may result in serious injury/illness or even death. Fatalities from skin exposure to TMAH solutions as dilute as 25% have been recorded. Some occurred due to heart attack despite immediate decontamination and prompt medical care. Thus skin exposure to >1% TMAH over a few percent of the body must be treated as a life-threatening event. Thirteen cases of exposure were reported to Taiwan Poison Control Center between Jan 1986 and Aug 2009. Nine victims were exposed to solutions of 2.38% TMAH. Only one victim had a serious poisoning/intoxication. The key differentiator was % body surface area (BSA) affected. One worker with 28% of body surface contaminated developed muscle weakness, salivation, dyspnea, hyperglycemia, and 1st and 2nd degree burns. The victim required medical intervention with endotracheal intubation and intensive care. Other individuals, with 1% to 18% of BSA affected displayed 1st or 2nd degree burns and required only mild supportive care. One individual, 5% BSA exposed, experienced muscle weakness.

TMAH concentration is the most important factor associated with serious poisoning intoxication and the % BSA also appears to be important. Differences in contact with skin and the effectiveness of PPE make a direct comparison difficult. However, the time to decontamination does not appear as important: the absorption through the skin may be very rapid. **The key is therefore to limit the exposure.**

5. Safety Precautions for TMAH Use

a) Training

Students and employees who handle TMAH must have read the Safety Data Sheet (SDS) and receive training on the hazards of TMAH from their respective department. They must know what to do in the event of a spill or an exposure incident. The SDS must always be kept within the immediate vicinity of the working area along with the SOP developed by the student/employee's department.

b) Ventilation / Fume Hood

Because TMAH can potentially generate toxic and corrosive fumes, it must always be handled under a certified working chemical fume hood. If ventilation is not sufficient, a respirator suitable for basic (alkali) vapors should be worn. Always contact EHS for fit-testing before using any kind of respirator.

c) Eye Protection

Splash goggles and a face shield MUST be worn when handling TMAH solutions.

d) Gloves

The disposable gloves may only provide brief protection and must be replaced if they become wetted. More protective gloves are the Sol-Vex, Stansolv or TRIonic glove models sold by MAPA. TRIonic clean room gloves provide excellent protection from TMAH exposure. **Table 2** shows some PPE breakthrough time.

Table 2: Permeation Testing Data Against 25% TMAH[1]

Material	Breakthrough time (min)
Ansell Sol-Vex® 37-165 gloves (22 mil)	>480
MAPA® Professional E-194 TRIonic® gloves (20 mil)	>480
Tychem® SL coveralls	>480

[1]Reported IBM exposure controls

e) Protection Clothing

A chemical apron over a lab coat or chemical smock with long sleeves MUST be worn when handling TMAH solutions, along with long pants, sleeves, and closed toe shoes/boots. **No exposed skin is allowed**.

f) Safe Work Practice

- Do NOT handle TMAH containing materials when working alone. Have lab buddy system in place.
- Avoid contact with the material.
- Wash hands and face thoroughly after working with material.
- Contaminated clothing should be removed and washed before re-use.

6. Storage, Spill and Waste Issues

a) Storage

The quantities of TMAH kept in storage should be kept to a minimum. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. TMAH should be stored under inert gas as it is sensitive to carbon dioxide.

TMAH is not compatible with oxidizing agents (such as perchlorates, peroxides, permanganates, chlorates, nitrates, chlorine, bromine and fluorine). TMAH reacts vigorously with strong acids.

b) Spills

In the case of a small spill, the spill can be cleaned by laboratory staff assuming that the correct equipment is present and that the staffs understands the hazards associated with TMAH.

1. Ventilate area of leak or spill.
2. Wear appropriate personal protective equipment as specified above.

3. Absorb on an inert absorbent; BDH Spillage absorption granules or J. T. Baker SOLUSORB® solvent adsorbent are recommended for spills of this product but other inert absorbents (*e.g.*, vermiculite, dry sand, earth) can also be used.
4. Wash site of spillage thoroughly with water and detergent.
5. Transfer all waste to a suitable container properly labelled as "Tetramethylammonium Hydroxide Waste".
6. Contact EHS (hazardouswaste@concordia.ca) to request an immediate pick-up of the containers of spilled product and contaminated absorbent material.

In the event of a large spill located outside a chemical fume hood, the spill must be cleaned by only personnel trained to handle hazardous materials:

1. Advise and warn co-workers.
2. Evacuate the area immediately.
3. Restrict the access to the area.
4. Notify Campus Safety and Prevention Services (CSPS) at **3717** or **514 848-3717**, providing them with the following information:
    a. Name of hazardous material
    b. Quantity involved
    c. Related health risks and precautions to be taken
5. Provide Safety Data Sheet (SDS) or appropriate documentation.

c) Waste Handling

Add the TMAH waste into the waste container inside the fume hood by using a funnel. TMAH waste should never be mixed with other organic wastes. It should be kept in clearly identified containers labelled "Tetramethylammonium Hydroxide Waste". Store the TMAH waste container away (segregate) from acids, acid waste and oxidizing chemicals/agents. Use secondary containment (Nalgene or polypropylene tray/tub) when storing the waste. Contact EHS (hazardouswaste@concordia.ca) to request a waste pick-up.

7. Emergency Procedures

a) Skin Contact

1. Remove contaminated clothing and immediately wash the affected area with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
2. Call CSPS at **3717** for emergency medical assistance.

b) Eye Contact

1. Immediately wash the affected eye with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
2. Do not allow the victim to rub or keep eyes closed.
3. Call CSPS at **3717** for emergency medical assistance.

c) Inhalation

1. Immediately move the victim to fresh air.
2. If breathing is difficult, administer oxygen.
3. Call CSPS at **3717** and ask for medical assistance.

d) Ingestion

1. Wash out the mouth thoroughly with water and give large quantity of water to drink.
2. While the victim is rinsing his/her month, someone should someone should call CSPS at **3717** and ask for medical assistance.
3. Do not induce vomiting.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) must be brought to the emergency room as the treating physician might be unaware of the treatment measures for TMAH. All TMAH incidents must be reported to your Supervisor and to Environmental Health & Safety. An injury/near-miss report must be filled for any incident involving tetramethylammonium hydroxide spill or exposure. If you have any concerns about the use of tetramethylammonium hydroxide at Concordia University, please contact EHS at **ehs@concordia.ca.**

Preparation date: November 2012

Revision dates: August 2016, July 2024

References (*Updated in July 2024*):

- SDSs: 1)Sigma-Aldrich Tetramethylammonium Hydroxide Pentahydrate SDS; 2) Sigma-Aldrich Tetramethylammonium Hydroxide (25-30 wt% in water) SDS; 3) Sigma-Aldrich Tetramethylammonium Hydroxide (10-25 wt% in Methanol) SDS.
- Stanford Environmental Health & Safety, Tetramethylammonium Hydroxide (TMAH) Fact Sheet and references therein – Consulted in July 2024.
- New Jersey Department of Health and Senior Services, Hazardous Substance Fact Sheet: Tetramethylammonium Hydroxide, October 2001 – Consulted in July 2024.
- Harvard University Laboratory Safety Guideline: Tetramethylammonium hydroxide (TMAH) – Consulted in July 2024.
- University of Ilinois Urbana-Champaign - Division of Research Safety, Tetramethylammonium hydroxide: Background and Overview of Hazards and references therein– Consulted in July 2024.
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- Wu, C.-L.; Su, S.-B.; Chen, J.-L.; Lin, H.-J.; Guo, H. R. Mortality from dermal exposure to Tetramethylammonium Hydroxide, *J. Occup Health* **2008**, *50*, 99-102.
- Yang, Y.; Kim, S. M.; Park, J. S. A case of cardiac arrest after dermal exposure to 2.38% tetramethylammonium hydroxide, *J. Kor. Soc. Emerg. Med.* **2022**, *33*, 3, 322-325.
- Chandra, T.; Zebrowski, J. P.; McClain, R.; Lenertz, L. Y. Generating Standard Operating Procedures for the manipulation of hazardous chemicals in academic laboratories. *ACS Chem. Health Saf.* **2021**, *28*, 19-24. https://dx.doi.org/10.1021/acs.chas.0c00092.