|  |
| --- |
| Standard Operating Procedure |
| Tetramethylammonium hydroxide (TMAH) solution |

*This is an SOP template and is not complete until: 1) lab specific information is entered into the box below 2) lab specific protocol/procedure is added to the protocol/procedure section and
3) SOP has been signed and dated by the PI and relevant lab personnel.*

 Print a copy and insert into your
*Laboratory Safety Manual* and *Chemical Hygiene Plan*.
Refer to instructions for assistance.

|  |  |
| --- | --- |
| School / Department: | Click here to enter text. |
| SOP Preparation Date: | Click here to enter a date. | SOP Approval Date: | Click here to enter a date. |
| Principal Investigator: | Click here to enter text. |
| Lab Manager Name: | Click here to enter text. |
| Laboratory Phone: | Click here to enter text. | Office Phone: | Click here to enter text. |
| Emergency Contact: | Click here to enter text. | Contact Phone: | Click here to enter text. |
| Laboratory locations covered by this SOP (building / room number): |
| Click here to enter text. |

|  |  |  |  |
| --- | --- | --- | --- |
| Type of SOP: |[ ]  Process |[x]  Hazardous Chemical |[ ]  Hazardous Class |

**Purpose**

Tetramethylammonium hydroxide (TMAH) is widely used in micro- or nanofabrication as an etchant or developer. TMAH is typically one of several ingredients in commercial etching / stripping mixtures, although it may be used alone in a water- or methanol-based solution.

**Uses:** Tetramethylammonium hydroxide (TMAH or TMAOH) is a quaternary ammonium salt with the molecular formula (CH3)4NOH. It can be used as an anisotropic etchant of silicon, generally at higher concentrations (25%). It is also used as a basic solvent in the development of acidic photoresist in the photolithography process, generally at lower concentrations (typically about 2.4%). It is also used as a surfactant in the synthesis of ferrofluid, to prevent agglomeration.

**Synonyms:** Tetramethylammonium hydroxide 20% in methanol; TMAH 25%; Methanaminium; Ammonium Tetramethyl Hydroxide

**Physical and Chemical Properties / Definition of Chemical Group**

|  |  |  |
| --- | --- | --- |
| CAS: | 75-59-2 |  |
| Class: | Corrosive & Toxic |
| Molecular Formula: | (CH3)4NOH |
| Form (physical state): | Liquid |
| Color: | Colorless to straw-colored |
| Solubility: | 100% in water |
| pH: | Very strong base, >13 @ 20°C |
| Boiling Point: | 60–65°C (140–149°F) |
| Odor: *Strong ammonia-like odor. Smells like dead fish if not pure, from Trimethlamine impurity.* |

**Potential Hazards / Toxicity**

While it has long been known to be very toxic if ingested, recent industrial experience indicates that skin exposure may result in serious injury or even death. There is no known antidote for TMAH poisoning through either ingestion, skin, or eye contact – immediate removal of the material using a safety shower /eyewash is critical. Hospitalization and respiratory support has been shown to be somewhat effective. Since 2007, there have been several recorded fatalities from skin exposure to TMAH solutions. At least three of the recorded fatalities occurred due to heart attack despite immediate decontamination and prompt medical care. Thus skin exposure to >1% TMAH solutions over a few percent of the body must be treated as a life-threatening event. SDSs may be out of date and not properly describe this high dermal toxicity. *SESHA National Symposium, April 2018.*

TMAH solution is a strong base, similar to sodium hydroxide. The Tetramethylammonium ion can damage nerves and muscles, causing difficulties in breathing and possibly death in a short period of time after exposure by contact, even with only a small amount of a small concentration. It is structurally similar to acetylcholine, an important peripheral neurotransmitter at both the neuromuscular junction and autonomic ganglia. This structural similarity is reflected in its mechanism of toxicity - it binds to and activates the nicotinic and muscarinic acetylcholine receptors, although the response may subsequently densentize in the continued presence of this agonist. The action of tetramethylammonium is most pronounced in autonomic ganglia, and so tetramethylammonium is traditionally classed as a ganglion-stimulant drug. The ganglionic effects may contribute the deaths that have followed accidental industrial exposure, although the "chemical burns" induced by this strong base are also severe and play an essential role in the toxicity of the material.

**POISON! DANGER! CORROSIVE. SKIN CONTACT MAY BE FATAL. MAY BE FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. CAUSES BURNS TO ANY AREA OF CONTACT. VAPOR HARMFUL. FLAMMABLE LIQUID AND VAPOR (METHANOL-BASED SOLUTIONS). MAY CAUSE BLINDNESS. CANNOT BE MADE NONPOISONOUS.**

Exposure may result in intense burning of the eyes, nose, throat, lungs and skin. Experimental studies have indicated that TMAH is a weak inhibitor of acetylcholinesterase and acts as a cholinergic (muscarinic and nicotinic) agonist. Depending on the level and duration of exposure, signs and symptoms may include blurred or double vision; pinpoint pupils; changes in heart rate and blood pressure; abdominal cramping, nausea and vomiting; diarrhea, excessive salivation sweating or bronchial secretions; urinary incontinence; muscle twitching, tremors or convulsions. Other symptoms consistent with cholinergic activity may also be observed.

|  |
| --- |
| **Potential Health Effects** |
| *Highly toxic by skin absorption, Highly toxic by ingestion, Corrosive – causes burns* |
| **Inhalation:** | May be harmful if inhaled. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract. |
| **Skin:** | May be fatal if absorbed through skin. Causes skin burns. |
| **Eyes:** | Causes severe eye burns. |
| **Ingestion:** | May be fatal if swallowed. |
| **Chronic exposure:** | Marked impairment of vision has been reported. Repeated or prolonged exposure may cause skin irritation. |
| **Aggravation of pre-existing conditions:** | Persons with pre-existing skin disorders or eye problems or impaired liver or kidney function may be more susceptible to the effects of the substance. |

**Personal Protective Equipment (PPE)**

When handling Tetramethylammonium hydroxide (TMAH) solutions, the minimum set of personal protective equipment includes:

* Safety goggles (not safety glasses)
* Disposable nitrile gloves
* A buttoned lab coat
* Full length pants
* Closed-toe shoes

**Note:** The disposable gloves may only provide brief protection and must be properly disposed and replaced if they become wetted. More protective gloves are the Stansolv or Tri-Ionic glove models sold by MAPA. Tri-Ionic clean room gloves provide excellent protection from TMAH exposure.

**Engineering Controls**

* Tetramethylammonium hydroxide (TMAH)must be handled under a chemical fume hood that has been inspected and certified by EH&S within the last one year.
* Do not open the sash above 18 inches (optimum level).
* Sash should also be used as a shield, by keeping the sash as low as possible that facilitates easy working condition in the fume hood.
* A thorough Process Hazard Review should be completed before this material is used. Specific steps should be identified to minimize the hazards identified in the review.

**First Aid Procedures**

**If inhaled…** Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately. Call 911 from a campus phone or (480) 965-3456. Call EH&S at (480) 965-1823.

**In case of skin contact…** Immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention immediately. Wash clothing before reuse. Thoroughly clean shoes before reuse. Call 911 from a campus phone or (480) 965-3456 from a cell phone. Call EH&S at (480) 965-1823.

**In case of eye contact…** Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately. Call 911 from a campus phone or (480) 965-3456 from a cell phone. Call EH&S at (480) 965-1823.

**If swallowed…** If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention immediately. Call 911 from a campus phone or (480) 965-3456 from a cell phone. Call EH&S at (480) 965-1823.

**Special Storage & Handling Requirements**

* Protect against physical damage to the container.
* Store in a cool, dry well-ventilated location, away from any potential fire hazard area.
* Outside or detached storage is preferred.
* Separate from incompatibles.
* Containers should be bonded and grounded for transfers to avoid static sparks (methanol-based solutions).
* Storage and use areas should be No Smoking areas (methanol-based solutions).
* Use non-sparking type tools and equipment, including explosion proof ventilation (methanol-based solutions).
* Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

**Stability:** Stable under ordinary conditions of use and storage. Readily absorbs CO2 from the air.
**Hazardous Decomposition Products:** Carbon oxides, nitrogen oxides and formaldehyde gas form when heated to decomposition.
**Hazardous Polymerization:** Will not occur.
**Incompatibilities:** Strong acids and oxidizing agents; attacks many plastics and rubber. May react with metallic aluminum and generate hydrogen gas.
**Conditions to Avoid:** Heat, flames, ignition sources and incompatibles.

**Label Precautions:**
Do not breathe vapor or mist.
Do not get in eyes, on skin, or on clothing.
Keep container closed.
Keep away from heat, sparks and flame.
Use only with adequate ventilation.
Wash thoroughly after handling.

**NOTE:** You should NOT handle TMAH containing materials when working alone. Have lab buddy system in place.

**Spill and Accident Procedure**

**Fire Fighting Measures**

**Fire:**

Water-based TNMAH solutions are not flammable

For methanol-based solutions –

Flash point: 12°C (54°F) closed-cup

Autoignition temperature: 470C (878F)

Flammable limits in air % by volume: *LEL: 6.7; UEL: 36*
Flammable Liquid and Vapor!

**Explosion:**
Above the flash point, explosive vapor-air mixtures may be formed (methanol-based solutions). Sealed containers may rupture when heated. Contact with strong oxidizers may cause fire. Sensitive to static discharge.
**Fire Extinguishing Media:**
Water spray, dry chemical, alcohol foam, or carbon dioxide. Water may be ineffective.
**Special Information:**
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode. Use water spray to blanket fire, cool fire exposed containers, and to flush non-ignited spills or vapors away from fire. Vapors can flow along surfaces to distant ignition source and flash back.

**Accidental Release Measures**

Notify all nearby personnel of the TMAH spill/leak. Keep unnecessary and unprotected personnel from entering. Isolate hazard area. Ventilate area of leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as specified in Section 8. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e.g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust to absorb spilled material. Do not flush to sewer! If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures.
J. T. Baker SOLUSORB® solvent adsorbent is recommended for spills of methanol-based solutions of this product.

**Decontamination / Waste Disposal Procedure**

**Label waste**

* Attach a completed ASU Hazardous Waste tag to all waste containers as soon as the first drop of waste is added to the container.

**Store waste**

* Store hazardous waste in closed containers, in secondary containment and in a designated storage location.
* Double-bag dry waste using sealable transparent bags.
* Waste must be under the control of the person generating and disposing of it.

**Dispose of waste**

* Dispose of regularly generated chemical waste within 90 days.
* Use EHS Assistant online hazardous waste pick-up request system.
* Contact ASU EH&S at (480) 965-1823 with questions.

**Protocol / Procedure**

**Laboratory-specific procedures**

Add your lab’s specific procedures in this section.

 Click here to enter text.

**IMPORTANT NOTE:** Any deviation from this SOP requires advance PI approval.

**Documentation of Training**

* Prior to conducting any work with tetramethylammonium hydroxide (TMAH), Principal Investigator or designee must provide to his/her laboratory personnel specific training in the hazards involved in working with this substance, work area decontamination, and emergency procedures.
* The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
* The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate/required laboratory safety training or refresher training within the last one year.

**I have read and understand the content of this SOP.**

|  |  |  |  |
| --- | --- | --- | --- |
| Employee Name | ASU Affiliate No. | Signature | Date |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |
| Click here to enter text. | Click here to enter text. |  | Click here to enter a date. |