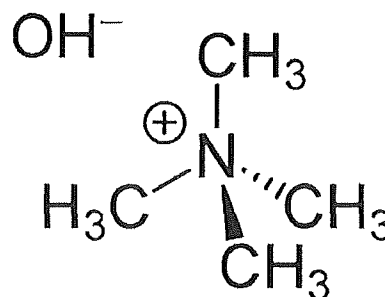


# TMAH

## Guidance on Prohibition

### WHAT IS TMAH?

Tetramethylammonium hydroxide (TMAH) inhibits the biological processes relied upon for wastewater treatment and water quality protection. TMAH is quaternary ammonium salt, and consists of a methylated nitrogen molecule. The CAS No. for TMAH is 75-59-2. In a wastewater stream, quaternary ammonium salts bind with different proteins in bacterial cells, inhibiting the bacteria's ability to remove various organic and ammonium-based compounds.



Physically, TMAH has a high solubility in water. As is common with the majority of quaternary ammonium salts, TMAH also has a high affinity to bind to solids when placed in a solution with solids and water.

### INDUSTRIAL USERS AND TMAH USES

A major use of the compound includes silicon etching that uses TMAH as the etchant for the production of electronics (these may include integrated circuits, flat panel displays, printed circuit boards, capacitors, sensors, and many other electronic components). TMAH is also used as an additive in the production of cleaners and formulated etches.

<b>SUGGESTED INDUSTRIAL USERS (IUS) TO INVESTIGATE AS A STARTING POINT*</b>	<ul style="list-style-type: none"><li>• Semiconductor manufacturers</li><li>• Electronic manufacturers</li><li>• IUs that test/repair any electronic components</li><li>• Metal Finishers</li><li>• Chemical Manufactures</li><li>• Soap and Detergent Manufacturers</li><li>• Centralized Waste Treaters</li></ul>
<b>SUGGESTED INVESTIGATIVE TECHNIQUES</b>	<ul style="list-style-type: none"><li>• Inspection</li><li>• Review Chemical Lists</li><li>• Review SDS's</li><li>• Sample IUs and/or City Interceptors</li></ul>
<b>*Documentation from past required IU surveys are a good source to identify potential contributors who are not currently permitted.</b>	

# LAB ANALYSIS METHODOLOGIES

## Understanding TMAH's Affinity for Solids

The physical properties of TMAH require measurement of the compounds in both the aqueous and solids phase to understand the full concentration in a wastewater stream. When TMAH is used for industrial processing, it is typically added as a dissolved compound in a liquid stream, and can therefore be measured as a soluble compound. However, when the industrial water containing TMAH comes in contact with municipal wastewater that contains a high concentration of particulate organic substances, the TMAH binds to the particulate organic substances. Due to this attraction to organics, if soluble TMAH is measured in a solution before and after contact with wastewater solids, a significant decrease in the measured TMAH will occur in the liquid phase. This is due to the fact that TMAH will quickly bind to the particulate organic substances, transferring the TMAH from the aqueous phase to the solids phase in the wastewater sample. TMAH still exhibits inhibitory effects in biological digestion in the solids phase, and therefore still impacts the performance of wastewater treatment facilities.

## Important Consideration when Choosing a Lab to Conduct TMAH Analysis

To account for this partitioning between aqueous and solid phases in a sample, it is critical that total TMAH be measured for all sampling related to TMAH detection in wastewater systems. Total TMAH measurement requires quantification of the aqueous and solids phase TMAH in a sample. This can be completed by extracting the TMAH bound to the sample solids, and then measuring the total TMAH present in solution after the extraction.

There is currently no EPA approved method in 40 CFR Part 136 for TMAH. TRA cannot recommend a specific laboratory for the analysis of TMAH. However, a description of the methodology used by TRA for its investigation for total TMAH (Soluble plus Non-Soluble) is included in Appendix A.

# PRETREATMENT PROGRAM

## REQUIRMENTS

TRA has reviewed all applicable Pretreatment Industrial Wastewater Ordinances for the CRWS Contracting Parties. All Contracting Parties have the appropriate legal authority to prohibit TMAH since the compound has been identified as a major contributor to the inhibition of treatment capabilities at the TRA Central Regional Wastewater System plant. Without this prohibition of TMAH, TRA-CRWS could potentially violate its permit to discharge with the Texas Commission on Environmentally Quality (TCEQ). TRA's Approved Pretreatment Program requires that Industrial User's must be informed about requirements for compliance with the Pretreatment Program. Therefore, the Industrial Users in your jurisdiction must be notified about this prohibition.

### **For TRA to Stay Compliant with the Approved Pretreatment Program**

Notification must be conducted with industrial users informing them of the prohibition on TMAH discharges and reason why. This notification must be conducted with significant industrial users (SIUs) and Non-Significant Industrial Users (Non-SIUs).

<b>SIU NOTIFICATION</b>	<ul style="list-style-type: none"> <li>• Send written notification to SIUs</li> </ul> <p style="text-align: center;"><b>AND</b></p> <ul style="list-style-type: none"> <li>• Send TRA a copy of the notification</li> </ul>
<b>NON-SIU NOTIFICATION</b>	<ul style="list-style-type: none"> <li>• Utilize public notification procedures</li> </ul> <p style="text-align: center;"><b>OR</b></p> <ul style="list-style-type: none"> <li>• Send written notification to Non-SIUs</li> </ul> <p style="text-align: center;"><b>AND</b></p> <ul style="list-style-type: none"> <li>• Send TRA a copy of the notification</li> </ul>

# APPENDIX A

## Methodology Used by TRA for Its Investigation for Total TMAH

### **Quaternary Ammonium Surfactant Extraction Procedure**

For the extraction of the total QACs the pH of the reaction solution was adjusted with phosphate buffer solution to 8.0. A 5-ml volume of an aqueous solution containing 0.01 M buffer solution and appropriate amounts of wastewater was mechanically shaken with 5 ml of chloroform for 20 min. After phase separation, the sample was filtered to remove any residual solids. The sample was then run using the HPLC method.

For free (non-adsorbed) QACs, the sample was filtered before the chloroform was added to the aqueous phase.

### **Cationic Surfactants by HPLC**

**Column: Acclaim Surfactant, 5  $\mu$ m**

**Dimensions: 4.6  $\times$  150 mm**

**Mobile Phase: (A) Acetonitrile**

**(B) 1% acetic acid (v/v)**

**Gradient:**

<b>Time (min)</b>	<b>A</b>	<b>B</b>
-		
<b>12</b>	20	80
<b>0</b>	20	80
<b>25</b>	80	20

**Temperature: 30  $^{\circ}$ C**

**Flow Rate: 1 mL/min**

**Inj. Volume: 10  $\mu$ L**

**Detection: UV 225 nm**