Applied Microbiology
&
Biotechnology Laboratory

"sustainable is attainable"

Standard Operating Procedure

AMBL-104-A

Prepared:	7/2/2017
Revised:	
Prepared by:	Terry E. Baxter
Reviewed by:	

Hardness by EDTA Titration

METHOD SUMMARY

This SOP describes the procedure for measuring hardness by titration with standard EDTA solution to endpoint indicated by a color change. This method is based on Method 2340 C of *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition.

ENVIRONMENTAL HEALTH AND SAFETY

Hazards Assessment: This method involves the use of chemicals and solutions that can present specific hazards if handled improperly. Typically the amounts of chemicals used are small. The specific hazards associated with these chemicals and solutions are as follows.

Skin Contact: Ammonium Chloride; causes irritation with symptoms that include redness, itching, and pain. EDTA disodium salt dihydrate; causes irritation. Ammonium Hydroxide and Buffer solution; causes irritation and burns. EDTA titrant 0.01M; may cause slight irritation.

Eye Contact: Ammonium Chloride; causes irritation, redness, and pain. EDTA disodium salt dihydrate; causes serious irritation. Ammonium Hydroxide and Buffer solution; releases vapors that causes irritation and splashes will cause strong irritation or burns, redness and pain, and the possibility of permanent blindness. EDTA titrant 0.01M; may cause slight irritation.

Ingestion: Ammonium Chloride; causes irritation to the gastrointestinal tract with symptoms that may include nausea, vomiting and diarrhea. EDTA disodium salt dihydrate; considered harmful if swallowed. Ammonium Hydroxide and Buffer solution; considered toxic and fatal if more than 3 or 4 mL is ingested, may cause corrosion to the esophagus and stomach with symptoms that include pain in mouth, chest and abdomen accompanied by coughing and vomiting, and possible collapse.

Inhalation: Ammonium Chloride; causes irritation to respiratory system with symptoms that may include coughing, shortness of breath. EDTA disodium salt dihydrate; may cause respiratory irritation. Ammonium Hydroxide and Buffer solution; causes respiratory tract irritation, although high vapor concentrations can cause burns, swelling and even death.

Safety Equipment and Engineering Controls: This method requires that the hardness buffer solution be added to the sample in a fume hood because of the ammonia fumes that are generated when handling the buffer solution. An eye wash station and a shower must be located nearby.

Personal Protective Equipment (PPE): This method requires the use of the following PPE.

Gloves (nitrile, PVC or neoprene)

Safety goggles or glasses

Laboratory coat

Analysis-derived Wastes and Disposal:

Waste Generated	Hazardous (Y / N)	Disposal
This procedure generates small volumes of sample wastes that have a pH value of approximately 10.	N	May be disposed in sink.
Ammonia buffer solution will be considered a waste after one month from the preparation date or when formation of precipitate is noticed. The pH of this solution when fresh is typically about 11.6 (which is > 2 and < 12.5).	N	Any solution that may not be saved for recovery should be disposed as a hazardous waste. Do not dispose in the sink.

METHOD DESCRIPTION

1.0 Introduction and Applicability

Hardness is the presences of dissolved calcium, magnesium and other dissolved polyvalent metal cations in water that can consume soaps used in washing operations and that cause scale deposits in heated water systems such as water heaters and boilers, heat exchangers, and in a number of other industrial and domestic equipment and pipes. Water hardness is dominated by the presence of calcium and magnesium cations because of extensive contact that water has with soil and rock formations containing of these cations. Because of this, total hardness is

typically defined as the sum of calcium and magnesium cation concentrations and is expressed in mg/L as calcium carbonate ($CaCO_3$). Because these cations can be associated with bicarbonates and carbonates in solution, total hardness may consist of a "carbonate hardness" and a "non-carbonate hardness," that are defined by its relative relationship with alkalinity.

This method is applicable for measurement of hardness in natural waters, including groundwater, municipal drinking water, and pretreated polluted waters and wastewaters.

2.0 Apparatus

a. Magnetic stirrer and stir bar
b. Wide-mouth Erlenmeyer flask, 125-mL
c. Buret, 50-mL, for standard EDTA titrant
d. Pipets, volumetric

3.0 Reagents

a. Standard calcium solution, primary standard prepared according to procedure given in Method 2340 C.2.e (*Standard Methods*) and adjust the pH to about 5.1 as described. Use 15 mL of this prepared solution (1 mL = 1.00 mg as $CaCO_3$) to standardize the EDTA titrant (calculate and express as mg $CaCO_3$ per mL of EDTA titrant).

b. Standard EDTA 0.01M titrant solution prepared according to procedure given in Method 2340 C.2.d (*Standard Methods*).

c. Buffer solution prepared according to procedure given in Method 2340 C.2.a (*Standard Methods*).

d. Complexing inhibitor solution (sodium sulfide) prepared as needed according to procedure given in Method 2340 C.2.b.2 (*Standard Methods*).

e. ManVer 2 hardness indicator (Hach, Cat No. 92899) and CalVer 2 calcium indicator (Hach, Cat. No. 94799).

4.0 Procedure

a. Read Method 2340 Hardness (*Standard Methods*).

b. Equilibrate the sample's temperature with the room's temperature and using a volumetric pipet transfer 25 mL of sample to a 125-mL flask. Add distilled water to bring the total volume up to about 50-mL.

c. Fill a clean buret with 0.01M EDTA titrant, making sure that there is no air space in the stopcock or the tip of the buret. Record the initial buret reading; read at the bottom of the meniscus.

d. Either place a stir bar in the flask (avoid splashing) and place the flask on the magnetic stirrer or you may mix the lash by swirling it using your hand. If using the magnetic stirrer, adjust the speed to gently stir the contents of the flask to avoid creating a vortex.

e. In the fume hood, add 1 to 2 mL of buffer solution and mix (or swirl). Replace and tighten the cap on the buffer solution bottle. If you are unsure that the sample pH is at 10.0 to 10.1, measure the pH (SOP 205A). Rinse the body of the electrode so that any sample remaining on the electrode is returned back into the flask.

f. Add the entire contents of one ManVer 2 indicator packet or one CalVer 2 indicator packet, depending on whether total hardness or calcium hardness is being measured, and mix (or swirl).

g. Continue mixing (or swirling) and begin adding EDTA titrant to the sample until the color changes from red to blue. Steadily add the titrant until the reddish color begins to disappear, and then slowly add titrant drop-by-drop to reach the endpoint.

h. If the color change is not sharp, either the indicator has deteriorated or 1-mL of the complexing inhibitor needs to be added.

i. This titration must be completed in less than 5 minutes to minimize precipitation of calcium.

j Record the final buret reading.

5.0 Calculation and Reporting

a. Calculate hardness

Hardness (EDTA), as mg/L $CaCO_3 = \frac{A \times T \times 1{,}000}{S}$

where A = mL of EDTA titrant used

T = Titer of EDTA titrant, mg CaCO3 per mL of EDTA titrant

S = mL of sample volume

b. Report as "Total Hardness (EDTA) = ____ mg/L as $CaCO_3$"

or as

"Calcium Hardness (EDTA) = ____ mg/L as $CaCO_3$"

c. Hardness due to magnesium is determined by calculation,

$$\text{Magnesium Hardness} = \text{Total Hardness - Calcium Hardness}$$

6.0 Quality Control

Standardize the 0.01M EDTA titrant monthly and use the new titer when calculating hardness. Prepare new buffer solution if it fails to provide a pH

of 10.0 to 10.1 or if precipitates are noticed or after one month from the previous preparation date. Check the inhibitor solution before use and if precipitates are noticeable, prepare a new solution. Perform one duplicate sample measurement for each hardness type and for every 20 or fewer samples analyzed.

7.0 Bibliography

1. Eugene W. Rice, Rodger B. Baird, Andrew D. Eaton, and Lenore S. Clesceri (2012) *Standard Methods for the Examination of Water and Wastewater*. APHA, Washington, DC, 22nd Edition.