



# 16

chapter

## Water Hardness Testing by Complexometric Determination of Calcium

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## 16.1 INTRODUCTION

### 16.1.1 Background

Ethylenediaminetetraacetate (EDTA) complexes with numerous mineral ions, including calcium and magnesium. This reaction can be used to determine the amount of these minerals in a sample by a complexometric titration. Endpoints in the titration are detected using indicators that change color when they complex with mineral ions. Calmagite and eriochrome black T (EBT) are such indicators that change from blue to pink when they complex with calcium and magnesium. In the titration of a mineral-containing solution with EDTA, the solution turns from pink to blue at the endpoint with either indicator. The pH affects a complexometric EDTA titration in several ways and must be carefully controlled. A major application of EDTA titration is testing the hardness of water, for which the method described is an official one (Standard Methods for the Examination of Water and Wastewater, Method 2340C; AOAC Method 920.196).

Hardness of water also can be tested by a more rapid test strip method. Such test strips are available from various companies. The strips contain EDTA and an indicator chemical to cause a color change when the calcium and magnesium in water react with the EDTA.

### 16.1.2 Reading Assignment

Ward, R.E., and Legako, J.F. 2017. Traditional methods for mineral analysis. Ch. 21, in *Food Analysis*, 5th ed. S.S. Nielsen (Ed.), Springer, New York.

### 16.1.3 Objective

Determine the hardness of water by EDTA titration and with Quantab® test strips.

## 16.2 EDTA TITRIMETRIC METHOD FOR TESTING HARDNESS OF WATER

### 16.2.1 Principle of Method

Ethylenediaminetetraacetic acid (EDTA) forms a Stable 1:1 complex with calcium or magnesium at pH 10. The metal ion indicators, calmagite and eriochrome black T (EBT), are pink when complexed to metal ions but blue when no metal ions are complexed to them. The indicators bind to metal ions less strongly than does EDTA. When the indicator is added to a solution containing metal ions, the solution becomes pink. When EDTA is added as titrant to the mineral-containing sample, metal ions preferentially complex with the EDTA, leaving the indicator without a metal ion to complex. When enough EDTA has been titrated to complex with all the metal ions present, the indicator

appears blue. This blue color is the endpoint of the titration. The volume and concentration of the EDTA in the titration are used to calculate the concentration of calcium in the sample, which is expressed as mg calcium carbonate/l. Stoichiometry of the reaction is 1 mol of calcium complexing with 1 mol of EDTA.

### 16.2.2 Chemicals

	CAS no.	Hazards
Ammonium chloride (NH <sub>4</sub> Cl)	12125-02-9	Harmful
Ammonium hydroxide (NH <sub>4</sub> OH)	1336-21-6	Corrosive, dangerous for the environment
Calcium carbonate (CaCO <sub>3</sub> )	471-34-1	
Calmagite [3-Hydroxy-4-(6-hydroxy- <i>m</i> -tolylazo)naphthalene-1-sulfonic acid]	3147-14-6	
Ethylenediaminetetraacetic acid, disodium salt (Na <sub>2</sub> EDTA · 2H <sub>2</sub> O)	60-00-4	Irritant
Hydrochloric acid, concentrated (HCl)	7647-01-0	Corrosive
Magnesium chloride, hexahydrate (MgCl <sub>2</sub> · 6H <sub>2</sub> O)	7791-18-6	
Magnesium sulfate, heptahydrate (MgSO <sub>4</sub> · 7H <sub>2</sub> O)	10034-99-8	

### 16.2.3 Reagents

(\*\*It is recommended that these solutions be prepared by the laboratory assistant before class.)

- Buffer solution\*\*  
Dissolve 16.9 g NH<sub>4</sub>Cl in 143 mL concentrated NH<sub>4</sub>OH. In 50 mL deionized distilled (dd) water, dissolve 1.179 g Na<sub>2</sub>EDTA · 2H<sub>2</sub>O (analytical reagent grade) and either 780 mg MgSO<sub>4</sub> · 7H<sub>2</sub>O or 644 mg MgCl<sub>2</sub> · 6H<sub>2</sub>O. Combine these two solutions with mixing and dilute to 250 mL with dd water. Store in tightly stoppered Pyrex or plastic bottle to prevent loss of ammonia (NH<sub>3</sub>) or pickup of carbon dioxide (CO<sub>2</sub>). Dispense this buffer solution with a repipette system. Discard buffer when 1–2 mL added to a sample fails to give pH 10.0 ± 0.1 at the endpoint of the titration.
- Calcium standard solution, 1.00 mg CaCO<sub>3</sub>/mL\*\* (modified from official method; omit use of methyl red indicator)  
Use primary standard or special reagent that is low in heavy metals, alkalis, and magnesium. Dry CaCO<sub>3</sub> at 100 °C for 24 h. Accurately weigh

ca. 1.0 g  $\text{CaCO}_3$ . Transfer to a 500-mL Erlenmeyer flask. Place a funnel in the neck of the flask and add HCl (1:1, conc. HCl:H<sub>2</sub>O) a little at a time, until all the  $\text{CaCO}_3$  has dissolved (make sure all the  $\text{CaCO}_3$  in the neck of the flask has been washed down with HCl). Add 200 mL dd water and boil a few minutes to expel  $\text{CO}_2$ . Cool. Adjust to pH 3.8 with 3M  $\text{NH}_4\text{OH}$  or HCl (1:1, conc. HCl : H<sub>2</sub>O), as required. Transfer quantitatively to a 1-L volumetric flask and dilute to volume with dd water (1 mL = 1.00 mg  $\text{CaCO}_3$ ).

- EDTA standard solution, 0.01 M  
Weigh 3.723 g  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ . Dilute to 1 L with dd water. Store in polyethylene (preferable) or borosilicate glass bottles. Standardize this solution using the calcium standard solution as described in the Procedure.
- Hydrochloric acid, 1:1 with water\*\*  
To 10 mL of dd water, add 10 mL concentrated HCl. Mix carefully.
- Calmagite\*\*  
Dissolve 0.10 g calmagite in 100 mL dd water. Use 1 mL per 30 mL solution to be titrated. Put in bottle with eye dropper.

#### 16.2.4 Notes

In this experiment, calmagite will be used as the indicator dye rather than EBT. Unlike EBT, calmagite is stable in aqueous solution. Calmagite gives the same color change as EBT, but with a sharper endpoint.

To give a satisfactory endpoint, magnesium ions must be present. To ensure this, a small amount of neutral magnesium salt is added to the buffer.

The specified pH of  $10.0 \pm 0.1$  is a compromise situation. With increasing pH, the sharpness of the endpoint increases. However, at high pH, the indicator dye changes color and there is risk of precipitating calcium carbonate ( $\text{CaCO}_3$ ) or magnesium hydroxide. The tendency toward  $\text{CaCO}_3$  precipitation is the reason for the titration duration time limit of 5 min.

Fading or indistinct endpoints can be caused by interference from some metal ions. Certain inhibitors can be added before titration to reduce this interference, but the inhibitors specified are toxic (i.e., sodium cyanide) or malodorous. Magnesium salt of 1,2-cyclohexanediaminetetraacetic acid ( $\text{MgCDTA}$ ), which selectively complexes heavy metals, may be substituted for these inhibitors. However, for samples with high concentrations of heavy metals, a non-EDTA method is recommended. In this experiment, inhibitors or  $\text{MgCDTA}$  will not be used.

#### 16.2.5 Hazards, Precautions, and Waste Disposal

Adhere to normal laboratory safety procedures. Wear gloves and safety glasses at all times. The buffer solu-

tion, which contains ammonium hydroxide, should be disposed of as hazardous waste. Other wastes likely may be put down the drain using a water rinse, but follow good laboratory practices outlined by environmental health and safety protocols at your institution.

#### 16.2.6 Supplies

(Used by students)

- Buret, 25 or 50 mL
- 9 Erlenmeyer flasks, 125 mL
- Funnel (to fill buret)
- Graduated cylinder, 50 mL
- 3 Graduated cylinders, 25 mL
- (Graduated cylinder of larger volumes may be necessary, for example, 100 mL or larger; size to be determined by trial in Sect. 16.2.8.2)
- Mechanical pipettor, 1000  $\mu\text{L}$ , with plastic tips
- Pasteur pipette and bulb
- Spatula
- Volumetric flask, 1000 mL
- Volumetric pipette, 10 mL
- Weighing paper/boat

#### 16.2.7 Equipment

- Analytical balance
- Drying oven, 100 °C
- Hot plate
- pH meter

#### 16.2.8 Procedure

(Modified from Method 2340 Hardness, *Standard Methods for the Examination of Water and Wastewater*, 22nd ed.) (Instructions are given for analysis in triplicate.)

##### Standardization of EDTA Solution

1. Pipette 10 mL of calcium standard solution into each of three 125-mL Erlenmeyer flasks.
2. Adjust to pH  $10.0 \pm 0.05$  with buffer solution. (If possible, do this pH adjustment with the buffer in an operating hood, due to its odor.) As necessary, use the HCl solution (1:1) in pH adjustment.
3. Add 1 mL of calmagite to each flask, and then titrate each flask with EDTA solution slowly, with continuous stirring, until last reddish tinge disappears, adding last few drops at 3–5 s intervals. Color at endpoint is blue in daylight and under daylight fluorescent lamp. Color may first appear lavender or purple, but will then turn to blue. Complete titration within 5 min from time of buffer addition.
4. Record the volume of EDTA solution used for each titration.

### Titration of Water Sample

1. Dilute 25 mL tap water sample (or such volume as to require <15 mL titrant) to ca. 50 mL with dd water in 125-mL Erlenmeyer flask. For tap distilled water, test 50 mL, without dilution. Prepare samples in triplicate [Official method recommends the following: For water of low hardness (<5 mg/L), use 100–1000 mL specimen, proportionately larger amounts of reagents, micro-buret, and blank of distilled water equal to specimen volume.]
2. Adjust pH to  $10 \pm 0.05$  as described in Sect. 16.2.8.1, Step 2.
3. Titrate each sample with EDTA standard solution slowly, as described in Sect. 16.2.8.1, Step 3, for standardization of EDTA solution.
4. Record the volume of EDTA solution used for each titration.

### 16.2.9 Data and Calculations

Calculate molarity of calcium standard solution:

Molarity of calcium solution =

$$\frac{\text{g CaCO}_3}{(100.09 \text{ g/mol})(\text{liter solution})} = \text{mol calcium/L}$$

Standardization of EDTA solution:

Rep	Buret start (mL)	Buret end (mL)	Volume titrant (mL)	Molarity
1				
2				
3				
				$\bar{X} =$
				SD =

Calculate molarity of EDTA solution:

mol calcium = mol EDTA

$$M_1 V_1 = M_2 V_2$$

$$(M_{\text{Ca solution}})(V_{\text{Ca solution,L}})$$

$$= (M_{\text{EDTA solution}})(V_{\text{EDTA solution,L}})$$

Solve for  $M_{\text{EDTA solution}}$

Titration of water sample with EDTA solution:

Rep	Dilution	Buret start (mL)	Buret end (mL)	Volume titrant (mL)	g Ca/L	mg CaCO <sub>3</sub> /L
1						
2						
3						
					$\bar{X} =$	$\bar{X} =$
					SD =	SD =

Calcium content of water sample (g Ca/L and g CaCO<sub>3</sub>/L):

mol calcium = mol EDTA

$$M_1 V_1 = M_2 V_2$$

$$(M_{\text{Ca in sample}})(V_{\text{sample, liter}}) =$$

$$(M_{\text{EDTA solution}})(V_{\text{EDTA solution used in titration, L}})$$

Solve for  $M_{\text{Ca in sample}}$ :

$$M_{\text{Ca in sample}} \times 40.085 \text{ g Ca/mol} = \text{g Ca/L}$$

$$(\text{g Ca/L})(100.09 \text{ g CaCO}_3 / 40.085 \text{ g Ca})$$

$$\times (1000 \text{ mg/g}) = \text{mg CaCO}_3 / \text{L}$$

### 16.2.10 Questions

1. If a sample of water is thought to have a hardness of approximately 250 mg/L CaCO<sub>3</sub>, what size sample (i.e., how many mL) would you use so that you would use approximately 10 mL of your EDTA solution?
2. Why were you asked to prepare the CaCl<sub>2</sub> solution by using CaCO<sub>3</sub> and HCl rather than just weighing out CaCl<sub>2</sub>?
3. In this EDTA titration method, would overshooting the endpoint in the titration cause an over- or underestimation of calcium in the sample? Explain your answer.

## 16.3 TEST STRIPS FOR WATER HARDNESS

### 16.3.1 Note

All information given is for AquaChek test strips, from Environmental Test Systems, Inc., a HACH Company, Elkhart, IN. Other similar test strips could be used. Any anion (e.g., magnesium, iron, copper) that will bind the EDTA may interfere with the AquaChek test. Very strong bases and acids also may interfere.

### 16.3.2 Principle of Method

The test strips have a paper, impregnated with chemicals, that is adhered to polystyrene for ease of handling. The major chemicals in the paper matrix are calmagite and EDTA, and minor chemicals are added to minimize reaction time, give long-term stability, and maximize color distinction between levels of water hardness. The strips are dipped into the water to test for total hardness caused by calcium and magnesium. The calcium displaces the magnesium bound to EDTA, and the released magnesium binds to calmagite, causing the test strip to change color.

### 16.3.3 Chemicals

	CAS no.	Hazards
Calcium carbonate (CaCO <sub>3</sub> )	471-34-1	Harmful
Calmagite	3147-14-6	
Ethylenediaminetetraacetic acid, disodium salt (Na <sub>2</sub> EDTA · 2H <sub>2</sub> O)	60-00-4	Irritant
Hydrochloric acid, concentrated (HCl)	7647-01-0	Corrosive
Other proprietary chemicals in test strip		

### 16.3.4 Reagents

(\*\*It is recommended that this solution be prepared by the laboratory assistant before class.)

- Calcium standard solution, 1.000 mg CaCO<sub>3</sub>/mL\*\*  
Prepare as described in Sect.16.2.3, using CaCO<sub>3</sub> and concentrated HCl.

### 16.3.5 Hazards, Precautions, and Waste Disposal

No precautions are needed in use of the test strip. Adhere to normal laboratory safety procedures. Wastes likely may be put down the drain using a water rinse, but follow good laboratory practices outlined by environmental health and safety protocols at your institution.

### 16.3.6 Supplies

- AquaChek® Test Strips (Environmental Test Systems, Inc., a HACH Company, Elkhart, IN)
- 2 Beakers, 100 mL

### 16.3.7 Procedure

(*Note:* Test the same standard calcium solution as used in Sect. 16.2.8.1 and the same tap water and tap distilled water as used in Sect.16.2.8.2.)

1. Dip the test strip into a beaker filled with water or the standard calcium solution. Follow instructions on strip about how to read it, relating color to ppm CaCO<sub>3</sub>.
2. Convert ppm CaCO<sub>3</sub> as determined with the test strips to mg CaCO<sub>3</sub>/L and g Ca/L.

### 16.3.8 Data and Calculations

Sample	Rep (ppm CaCO <sub>3</sub> )			Rep (mg CaCO <sub>3</sub> /L)			Rep (g Ca/L)		
	1	2	3	1	2	3	1	2	3
Tap water									
Tap distilled water									
Standard Ca solution									

### 16.3.9 Question

1. Compare and discuss the accuracy and precision of the EDTA titration and test strip methods to measure calcium carbonate contents of the water samples and the calcium standard solution.

### RESOURCE MATERIALS

- Rice, EW, Baird RB, Eaton AD, Clesceri LS (eds) (2012) Standard methods for the examination of water and wastewater, 22nd edn, Method 2340. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, pp. 2-37 to 2-39
- Ward RE, Legako JF (2017) Traditional methods for mineral analysis. Ch. 21. In: Nielsen SS (ed) Food analysis, 5th edn. Springer, New York