# Determination of Total Hardness in Water by Automatic Titration

#### Introduction

Total hardness due to calcium and magnesium in water is determined using the preprogrammed method, T7 Total Hardness. Calcium and magnesium in the sample are titrated to the equivalence point using an ethylenediaminetetracetic acid (EDTA) titrant<sup>1,2,3</sup>. A copper ion selective electrode (ISE) is used to follow the titration, and a copper-EDTA (Cu-EDTA) reagent serves as the indicator. Calcium and magnesium are titrated first, then the copper of the indicator reagent. The abrupt change in the copper concentration signals the endpoint. The copper ISE provides improved titrations over the calcium ISE. The titration is sensitive to both calcium and magnesium and can go to lower concentrations.

## **Recommended Equipment**

Thermo Scientific<sup>™</sup> Orion Star<sup>™</sup> T930 Ion Selective Electrode (ISE) Titrator or T940 All-in-One Titrator or equivalent with a 20 mL burette

Thermo Scientific<sup>™</sup> Orion<sup>™</sup> 9629BNWP Copper (Cupric) Combination ISE (or equivalent)

Pipette: 10 mL graduated

Graduated cylinders: 100 & 500 mL

Volumetric flasks: 100 & 250 mL

Beakers: 150 and 500 mL



#### Orion Star T930 ISE Titrator with 20 mL burette

#### **Required Reagents and Solutions**

Titrant: Purchased or prepared EDTA, 0.01M (0.01N).

Reagent, Cu-EDTA: Ethylenediaminetetracetic acid copper (II) disodium salt (Cu-EDTA), molecular weight 397.74, CAS 39208-15-60. Purchased salt or prepared solution, 0.01M.

Ammonia Buffer, pH 10: Purchased or prepared. Do not use a buffer containing magnesium EDTA.

Standardizing Solution (optional): Orion 922006 standard calcium solution, 0.1M.

Soaking Solution: Orion 942906 copper (cupric) standard, 0.1M.



Reagent grade water (RGW).

Acid and base for pH adjustment: 1M hydrochloric acid (HCl) and 1M sodium hydroxide (NaOH).

Use suitable Personal Protective Equipment (PPE) as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

## **Titrator Setup**

Connect the electrode and the stirrer probe to the titrator. If not previously done, import the T7 Total Hardness preprogrammed method into the titrator from the "Methods screen". Rinse and fill the burette with titrant. See the titrator user manual for details on setting up the titrator.

If bubbles are visible in the tubing, dispense titrant (from the "Burette" screen) until the bubbles have been expelled. Tap the tubing to dislodge bubbles. Consider standardizing the titrant before titrating samples. See the "Titrant" section on page 4.

## Table 1

T7 Total Hardness Preprogrammed Parameters					
Electrode	Parameter				
Electrode Type	ISE-Titration				
ISE Type	Copper Cu2+				
Electrode Name	edit as desired				
Titrant	Parameter				
Titrant Name	EDTA				
Titrant ID	edit as desired				
Conc Input Mode	Standardization				
Nominal Concentration	0.01M				
Standardize Tech	Equivalence pt.				
Number of Endpoints	1				
Results Units	Μ				
Standardize Reaction Ratio	1				
Standard Name	Calcium				
Standard Amount	Fixed Volume, 5 mL				
Standard Concentration	0.01 M				
Pre-dose Titrant Volume	3.5 mL				

Max total titrant volume	6.5 mL		
Stand. Process Control	User Defined		
E	15.0 mV		
Vmin	0.05 mL		
Vmax	0.1 mL		
dE/dt	7 mV/min		
Tmin	5 seconds		
Tmax	5 seconds		
Threshold	100 mV/mL		
Pre-stir Duration	10 seconds		
Stir Speed	Fast		
Titrantion	Parameter		
Titration Technique	Equivalence pt.		
Number of Endpoints	1		
Titration Type	Direct Titration		
Blank Required	No		
Result Units	mg/L		
Reaction Ratio	1.000		
Sample MW	100.09 g/mol		
Sample Amount	Variable volume		
Pre-dose Titrant Volume	olume 3.5 mL		
Max total titrant volume	9 mL		
Titration Process Control	User Defined		
E	15.0 mV		
Vmin	0.1 mL		
Vmax	0.1 mL		
dE/dt	7 mV/min		
Tmin	5 seconds		
Tmax	5 seconds		
Threshold	50 mV/mL		
Prestir	5 seconds		
Stir Speed	Fast		
Sample ID	Manual		

#### **Reagents and Solutions Preparation**

- Cu-EDTA Reagent, 0.01M (0.01N): If preparing from the salt, dissolve 3.98g of EDTA copper (II) disodium salt in 1L of RGW.
- Ammonia Buffer, pH 10: If preparing ammonia buffer, dissolve 16.9 g ammonium chloride (NH4Cl) in 143 mL of concentrated ammonium hydroxide (NH4OH) in a 250 mL volumetric flask. Dilute to 250 mL with RGW. If necessary, adjust to pH 10.0 +/- 0.1 with 1M HCl or NaOH. Discard and prepare fresh when 1 mL of buffer diluted to 100 mL with RGW reads lower than pH 9.9.

- Soaking solution: Add 1 mL of Orion 942906, 0.1M copper standard to a 150 mL beaker. Add RGW to the 100 mL mark to prepare 0.001M copper soaking solution.
- Conditioning solution: Add RGW to the 100 mL mark in a 150 mL beaker. Add 1 mL of ammonia buffer, swirl briefly to mix, and 2 mL of Cu-EDTA reagent.
- Standardizing solution, 0.01M calcium: Pipet exactly 10.0 mL of Orion 922006, 0.1M calcium standard into a 100 mL volumetric flask. Add RGW to the mark and mix.

## **Electrode Preparation**

At the start of the day: Remove the electrode from soaking solution. Add electrode fill solution up to the bottom of the fill hole. Leave the fill hole open during testing. Rub the sensor surface gently with a moistened lint-free wiper. Place the electrode into a freshly prepared conditioning solution for 5 minutes prior to the first titration. Rinse thoroughly with RGW before and between titrations.

At the end of the day: Clean any foreign materials from the sensor by wiping with a moistened lint-free wiper. Thoroughly rinse the electrode with RGW and store in prepared soaking solution. Cover the fill hole when in storage.

## Sample Preparation

If the pH of the sample is not in the range of pH 4.5 to 10, adjust the pH into that range using 1M NaOH or HCI. Using a graduated cylinder or pipet, transfer an amount of the sample into a 150 or 500 mL beaker, according to the expected sample concentration. See Table 2 for guidance on recommended sample volumes. Record the volume used. If less than 100 mL of sample is placed in the beaker, add RGW to the 100 mL mark on the beaker. Add 1 mL of ammonia buffer, swirl briefly to mix, and add 2 mL of Cu-EDTA reagent.

## Table 2

Recommended sample volumes						
Sample Concentration (mg/L as CaCO3)	Sample Concentration (mmol/L as CaCO3)	Volume of Sample (mL)				
5.0*	0.050	400				
10*	0.10	200				
25	0.25	200				
50	0.50	100				
100	1.0	50				
200	2.0	25				
300	3.0	15				
400	4.0	10				
600	6.0	10				
800	8.0	5				

\*For concentrations <25 mg/L (0.25 mmol/L), see Method Modifications.

## **Sample Titration**

- 1. From the "Home" screen or the "Methods" screen, select option to run the saved method "Total Hardness".
- 2. Rinse the electrode, stirrer, and dispenser with RGW. Place the electrode, stirrer, and dispenser into the prepared sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample. Ensure that the electrode junction is immersed.
- 3. Start the titration. Enter the sample volume and sample ID when prompted
- Results are reported as total hardness, mg/L as CaCO3. For other results units, see Method Modifications on page 4.



Orion Star T930 ISE Titrator with 20 mL burette

#### Table 3

Sample Results						
Sample	Average	Average	RSD	Average Analysis Time		
Tap Water	94.4 mg/L	0.944 mmol/L	0.98 %	03:29 min*		
Hard Water	176.5 mg/L	1.764 mmol/L	0.24%	02:33 min*		
Soft Water	8.95 mg/L	0.0894 mmol/L	1.7%	02:34 min		

\*using a 3.5 mL predose



Figure 1. Tap Water



Figure 2. Soft Water

#### Range

This preprogrammed titration method covers a range of about 5 to 800 mg/L as CaCO3, when using 0.01 M EDTA titrant and the prescribed volume of sample.

#### **Method Modifications**

- For total hardness samples with an expected concentration of less than 25 mg/L as CaCO3
  - Copy the Total Hardness method and create a second method with a new name. In the new method, edit Titration, then change the predose to 0.5 mL and the max volume to 4.5 mL.
- For total hardness in units of mmol/L:
  - Edit the method, edit titration programming, and change the result units to mmol/L

#### Titrant

Over time, standard titrant solutions age and can change concentration. For higher accuracy, determine the exact concentration by standardizing the titrant. It is common to standardize on a weekly basis, but other standardization frequencies may be suitable.

- 1. Standardizing titrant
  - a. Pipet 5.0 mL standardizing solution, 0.01M calcium standard, into a clean 150 mL beaker. Add RGW to the beaker to the 100 mL mark. Add 1 mL of ammonia buffer, swirl to mix, and 2 mL of Cu-EDTA reagent.
  - b. Select the "Total Hardness" method. At the titration pre-check screen, select the standardize option.
  - c. Start the titration. Standardization results will be displayed at the end of the cycle.
  - d. Run 3 or more cycles for the most accurate results. The average and relative standard deviation (RSD) of the cycles are automatically calculated when completed.
  - e. The new standardized titrant concentration will automatically be saved and used for subsequent titrations.
  - f. If using more than one hardness method with the same titrant (e.g., using a second version for low level titrations), note the standardized titrant value, and update the titrant concentration value in the other method by manual entry in the "Titrant" program parameters.

## 2. Certified Standardized Titrant Solutions

g. Some customers may prefer not to standardize their titrant, instead choosing to purchase and use certified standardized titration solutions. In this case, edit the "Titrant" section of the method. Choose manual entry and enter the certified concentration and titrant ID (i.e., lot number, if desired).

## **Titrator and Electrode Care**

 Refer to the titrator and electrode user manuals for details on cleaning, storage, and maintenance recommendations to keep the titrator and electrode performing well. Main points for care are summarized below.

## **Daily care**

- If bubbles are visible in the titrator tubing, dispense titrant until bubbles have been expelled. Tap tubing to dislodge bubbles that stick.
- Add electrode fill solution up to the bottom of the fill hole and leave the fill hole open during measurement.
- Rub the copper sensor gently with a moistened lint-free wiper to keep the surface clean.
- Prepare conditioning solution.
- Before the first titration of the day, condition the electrode for 5 minutes using the freshly-prepared conditioning solution.
- Rinse electrode well with RGW before and between titrations.
- Storage: Thoroughly rinse the electrode with RGW and store in soaking solution. Cover the fill hole.

## Weekly or biweekly care

- Drain and replace the fill solution of the electrode.
- Change the storage solution of the electrode.
- Consider standardizing the titrant on a weekly basis, or more frequently, as desired.

## As needed

- For slow or drifty electrode response, soak 15 minutes in warm 1% laboratory detergent while stirring. Brush the sensor gently with a soft toothbrush. Rinse well with RGW afterward.
- If the electrode is still slow or drifty, polish the sensor surface gently with low-abrasive polishing paper per instructions in the electrode user manual. Rinse well and place in soaking solution.
- See the electrode user manuals for maintenance details.

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#### **Ordering Information**

Product	Description	Cat. No.
Titrator	Orion Star T930 Ion Titrator without electrode Orion Star T940 All-in-One Titrator without electrode	START9300 START9400
Electrode	Orion Cupric (Copper) Ion Selective Electrode	9629BNWP
Orion Solutions	Orion Cupric (Copper) standard solution, 0.1 M Orion Calcium standard solution, 0.1 M	942906 922006
Accessories	150 & 500 mL beakers 10 mL graduated pipet 100 & 500 mL graduated cylinders 100 & 250 mL volumetric flasks	
Reagents	EDTA titrant, 0.01 M (0.01 N). Ethylenediaminetetracetic acid (EDTA) copper (II) disodium salt, molecular weight 397.74, CAS 39208-15-60. Purchased salt or prepared solution, 0.01M. Ammonia Buffer, pH 10: Purchased or prepared. Do not use a buffer containing magnesium EDTA.	
Reagent Grade Water	Thermo Scientific <sup>™</sup> Barnstead <sup>™</sup> Smart2Pure <sup>™</sup> 12 UV Water Purification System	50129890*

\* Please contact a sales representative for support on ordering the best water purification system for your application, or find out more at thermofisher.com/purewater

 Standard Methods 2340 C., Hardness, EDTA Titrimetric Method. Rice, Eugene W., Baird, Rodger B., Eaton, Andrew D., Lenore S. Clesceri. 2012. Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association.

 ASTM D1126-12, Standard Test Method for Hardness in Water. ASTM International, West Conshohocken, PA, USA, 2012. www.astm.org.

 ISO 6059-1984, Water Quality – Determination of the sum of calcium and magnesium – EDTA titrimetric method. International Organization for Standardization, Geneva, Switzerland, 2017. www.iso.org.

#### In the United States:

#### In Canada:

For customer service, call 1-800-766-7000 To fax an order, use 1-800-926-1166 To order online: thermofisher.com

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