

# Determination of Calcium Hardness in Water by Automatic Titration

## Key Words

EDTA, complexometric, titrimetric, ASTM D1126, ASTM D511, ISO 6059, SM 2340C, SM 3500-Ca, magnesium, Orion 9720BNWP, Orion Star T930, Orion Star T940, titrator. Drinking water, process water, cooling water, boiler water, wastewater, surface water, environmental water, raw water.

## Introduction

Calcium Hardness in water is determined using the preprogrammed method, T10 Ca Hard. To determine calcium, sodium hydroxide is added to a sample to raise the pH to 12 to 13. The sample is then titrated to the equivalence point using ethylenediaminetetraacetic acid (EDTA) titrant. A calcium ion selective electrode (ISE) is used as the titration indicator, which gives a potentiometric change when all the calcium has been complexed by the EDTA. The calcium ISE overcomes problems typical of color indicators such as endpoints that are not clear and sharp, endpoint color changes that are subjective, and the need for careful lighting to determine the endpoint during titration.

## Recommended Equipment

Thermo Scientific™ Orion Star™ T930 Ion Titrator or T940 All-in-One Titrator or equivalent with a 20 mL burette.

Thermo Scientific™ Orion™ 9720BNWP Calcium electrode or equivalent.

Pipet: 10 mL graduated; 1.00 mL (optional for standardization)

Graduated cylinders: 100 mL and 250 mL

Beakers: 100 mL and 250 mL



Orion Star T930 ISE Titrator with 20 mL burette

## Required Reagents and Solutions

Titrant: Purchased or prepared EDTA titrant, 0.01M (10 mM).

Calcium Standard: Orion 92206 0.1M Calcium Standard. For preparation of storage solution and for standardizing titrant.

Water Hardness Standard (optional): Orion 923206 Water Hardness Standard, 100 mg/L (ppm).

Reagent Solutions: Purchased or prepared 1N (1M) Sodium Hydroxide; Prepared storage solution.

Reagent grade water (RGW).

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

## Titration Setup

Connect the electrode and the stirrer probe to the titrator. If not previously done, import the T10 Ca Hard preprogrammed method into the titrator through 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 Titrant section below.

## Electrode Preparation

At the start of the day, remove the electrode from storage solution. Add fill solution to the bottom of the fill hole. Leave the fill hole open during testing. Rinse thoroughly with RGW before and between titrations. At the end of the day, thoroughly rinse the electrode with RGW and store in storage solution. Cover the fill hole when in storage.

## Storage Solution Preparation

Place 5 mL of Orion 922006, 0.1M calcium standard into a 100 mL beaker and add RGW to the 50 mL mark to make a 0.01M storage solution. Store the calcium ISE in this solution. Prepare fresh on a weekly or biweekly basis.

## Sample Preparation

Using a graduated cylinder or pipet, accurately transfer an appropriate amount of the sample into a clean beaker. See Table 2 for guidance on recommended beaker size and sample volumes. Record the volume used. If the volume of sample is less than 50 mL, add RGW to the 50 mL mark on the side of the beaker. Add 2 mL of 1N NaOH to bring the pH above 12 (e.g., near 12.5). Proceed to Sample Titration.

Table 1

T10 Ca Hard Method: Preprogrammed Parameters	
Electrode	Parameter
Electrode Type	ISE-Titration
ISE Type	Calcium (Ca <sup>2+</sup> )
Electrode Name	edit as desired
Titrant	Parameter
Titrant Name	EDTA
Titrant ID	edit as desired
Conc Input Mode	Standardization
Nominal Concentration	10.0 mM
Standardize Tech	Equivalence Pt.
Number of Endpoints	1
Results Units	mM
Standardize Reaction Ratio	1
Standard Name	Calcium
Standard Amount	Fixed Volume, 1.0 mL
Standard Concentration	0.10 M
Pre-dose Titrant Volume	8 mL
Max total titrant volume	16 mL
Stand. Process Control	Routine
Pre-stir Duration	10 seconds
Stir Speed	Fast
Titration	Parameter
Titration Technique	Equivalence Pt
Number of Endpoints	1
Display Units	mV
Titration Type	Direct
Blank Required	No
Result Units	mg/L
Reaction Ratio	1
Sample Amount	Variable volume
Sample MW	100.1
Pre-dose Titrant Volume	2.0 mL
Max total titrant volume	4.0 mL
Titration Process Control	User Defined
$\Delta E$	15 mV
$\Delta V_{min}$	0.050 mL
$\Delta V_{max}$	0.050 mL
dE/dt	10 mV/min
Tmin	2 seconds
Tmax	10 seconds
Threshold	100
Prestir Duration	10 seconds
Stir Speed	Fast
Sample ID	Manual

**Table 2**

Recommended sample volumes			
Expected sample concentration (mg/L)	Sample amount (mL)	Beaker size (mL)	Add this volume of RGW to the beaker (mL)
15	200	250	---
50	60	100	---
100	30	100	To the 50 mL mark
200	15	100	To the 50 mL mark
300	10	100	To the 50 mL mark
500	6.0	100	To the 50 mL mark

**Sample Titration**

1. From the Methods screen, select option to run the saved method T10 Ca Hard.
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.
3. Start the titration. Enter the sample volume and sample ID when prompted.
4. Results reported are calcium hardness in mg/L CaCO<sub>3</sub>.

**Orion Star T930 ISE Titrator with 20 mL burette****Table 3**

Sample Results				
Sample	Results (mg/L as CaCO <sub>3</sub> )	% Recovery	RSD (n = 4)	Analysis Time (min:sec)
Hardness QC Standard	182.0	101%	0.23%	02:30 min
Tap Water	66.86	NA	0.87%	02:29 min
Low Hardness Standard	15.31	102%	1.2%	02:55 min

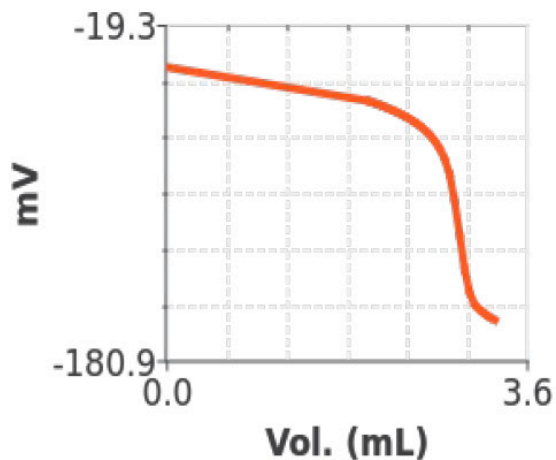


Figure 1. Calcium Hardness in Tap Water

### Range

This preprogrammed titration method covers a range of about 15 to 500 mg/L of Hardness, when using 0.01 M (10 mM) EDTA titrant and the prescribed volume of sample.

### 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 1.0 mL standardizing solution, 0.1M calcium standard, into a clean 100 mL beaker. Add RGW to the 50 mL mark on the side of the beaker. Add 2 mL of 0.1N NaOH.

b. 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. For the most accurate results, run 3 or more cycles. The average value and relative standard deviation (RSD) of the cycles are automatically calculated when titrations are completed.

e. The new standardized titrant concentration will automatically be saved and used for subsequent titrations for that method.

#### 2. Certified Standardized Titrant Solutions

a. 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 Conc. Input Mode = Manual and enter the certified concentration and titrant ID (i.e., lot number, if desired).

### Titration 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.
- Rinse electrode well with RGW before and between titrations.
- Storage: Thoroughly rinse the electrode with RGW and store in storage solution. Cover the fill hole.

### Weekly or biweekly care

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

### As needed

- For slow or drifty electrode response, soak the electrode in for 1 hour in RGW. Drain and replace the old filling solution, and soak the electrode for a few hours in freshly prepared storage solution. See the Storage Solution Preparation section above.
- See the electrode user manuals for maintenance details.



Orion Star T930 ISE Titrator with 20 mL burette

## Ordering Information

Product	Description	Cat. No.
Titrator	Orion Star T930 Ion titrator without electrode	START9300
	Orion Star T940 All-in-One Titrator without electrode	START9400
Electrode	Orion Calcium ISE Electrode	9720BNWP
Orion Solutions	Orion Optimum Results A filling solution	900061
	Orion Chloride standard solution, 0.1 M	922006
	Orion Water Hardness Standard (optional)	923206
Accessories	• Orion Electrode storage sleeve	810017
	• 100 & 250 mL beakers	
	• 100 & 250 mL graduated cylinders	
	• 10 mL graduated pipet	
	• 1.00 mL Pipete (optional for standardization)	
Reagents	• 0.01M EDTA titrant	
	• 1N (1M) Sodium Hydroxide	
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ Pro 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](http://thermofisher.com/purewater)

1. SM 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. [www.standardmethods.org](http://www.standardmethods.org)
2. ASTM D1126, Standard Test Method for Hardness in Water. ASTM International, West Conshohocken, PA, USA. [www.astm.org](http://www.astm.org).
3. 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](http://www.iso.org).
4. SM 3500-Ca B., Calcium, 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. [www.standardmethods.org](http://www.standardmethods.org)
5. ASTM D511, Standard Test Methods for Calcium and Magnesium in Water. ASTM International, West Conshohocken, PA, USA. [www.astm.org](http://www.astm.org).

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