

# Hanna Titration Procedure

Total Hardness in Water, Photometric Method



## Description

Method for the determination of total hardness ( $\text{CaCO}_3$ ) in water, following the photometric titration method to a color change endpoint with the HI932 Automatic Titrator. The result is expressed in **ppm (mg/L) of calcium carbonate ( $\text{CaCO}_3$ )**.

## Reference

Standard Methods for the Examination of Water and Wastewater, 2340 C. EDTA Titrimetric Method.

## Meter

- Automatic Potentiometric Titrator - [HI932](#)

## Electrodes

- 525 nm Photometric Electrode - [HI900601](#)

## Reagents

- 0.02 M EDTA Titrant (1 L) - [HI70449](#)
- Ammonium-Hydroxide/Ammonium-Chloride/EDTA-Magnesium Buffer Solution per 2340 C.2.a<sup>1</sup>
- 0.5% Eriochrome Black T (in Sodium Chloride) Color Indicator per 2340 C.2.c.
- Deionized Water - [HI70436](#)

## Accessories

- 50 mL Class A Pipette
- 5 mL Eppendorf Pipette Tips
- Eppendorf Pipette
- HI920-060 150 mL Plastic Beakers (20pcs)
- Scientific Balance
- Weigh Boats

## Device Preparation

- Connect the photometric electrode to the titrator.
- Press "Select Method" from the main screen. Use the arrow keys to highlight the 'Hardness Photometric' method and press "Select".
- Install a 25-mL burette with 0.02M EDTA (HI70449) on pump one and verify that no air bubbles are present in the burette or tubing. If necessary, prime the burette until all the air has been removed completely.  
For the determination of the exact concentration of the 0.02M EDTA, follow the method for 0.02M EDTA Titrant.  
For the determination of the exact concentration of the 0.02M EDTA, follow the method for 0.02M EDTA Titrant Concentration for Photometric EDTA Titer.

## Electrode Preparation

- Remove the electrode from the protective storage cap.
- Put the titrator into mV mode by pressing "Mode".
- Then, select analog board 1, and press "mV1".
- Fill a 120 mL beaker with 100mL deionized water.
- Submerge the electrode into the deionized water.
- Press "STIR" to gently stir the solution, ensuring the stir speed does not exceed 800 RPM.
- Remove the green protective cap from the electrode (it looks like a traditional electrode fill cap, and is located beneath the word "CAL").
- Use the provided calibration screwdriver to turn the calibration screw until the mV reading on the titrator reads  $1000 \pm 5$  mV.
- Press "Mode" and then "Titrator" to return to titration mode.
- **NOTE:** This calibration should be performed upon initial installation, and once per week thereafter.

<sup>1</sup> An Ammonium-Hydroxide/Ammonium-Chloride buffer can be substituted for the buffer with EDTA-Magnesium. For the purposes of automatic titration, the EDTA-Magnesium is not necessary..

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## Sample Preparation:

- Use a Class A glass pipette to transfer exactly 50.00 mL of sample to a clean beaker.<sup>2</sup>
- Using the 5 mL Eppendorf pipette, transfer 1.5 mL of the Ammonium-Hydroxide/Ammonium-Chloride buffer solution to your sample beaker.<sup>3</sup>
- Add 0.2 g of Eriochrome Black T Color Indicator mixture to the beaker.<sup>4</sup>
- Using deionized water, bring the volume of liquid up to submerge the electrode (approximately to the 75 mL mark), if necessary.

## Analysis

- Place the beaker under the stirrer assembly and lower it to immerse the photometric electrode and stirrer.<sup>5</sup> Ensure that the optical cell of the electrode is 5-6 mm below the surface.  
**NOTE:** The dispensing tip should be in contact with the surface of the sample (slightly submerged).
- Press "Start". The titrator will start the analysis.
- At the end of titration, when the equivalence point is reached, titration complete' will appear with the calcium carbonate concentration. The result is expressed as **total hardness as mg/L CaCO<sub>3</sub>**.
- Remove the photometric electrode and stirrer from the sample and rinse them thoroughly with deionized water.
- Record the result.

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<sup>2</sup> For ion-exchanger effluent or other softened water and for natural waters of low hardness, utilize a larger sample of 100 mL for titration and add proportionately larger amounts of buffer and indicator.

<sup>3</sup> The 1.5 mL buffer addition must increase the pH of the sample above pH 10; adjust the reagent volume for highly buffered samples, if necessary.

<sup>4</sup> Different types and formulations of colored indicators can be used for total hardness determination; see Section 2.C. of the reference method for more information.

<sup>5</sup> To avoid the generation of air bubbles, the stir speed should not exceed 800 RPM.