

Hardness, titrimetric, complexometric

Parameter and Code:
Hardness I-1338-85 (mg/L as CaCO_3): 00900

1. Application

This procedure is applicable to most natural and treated water, but the method fails conspicuously at times with acidic or polluted water that contains excessive amounts of heavy metals.

2. Summary of method

2.1 Disodium dihydrogen ethylenediamine-tetraacetate (Na_2EDTA) forms a slightly ionized, colorless, stable complex with alkaline earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths, but with them forms a deep-red complex that has a higher ionization constant than that of the Na_2EDTA complex. Hence, with Eriochrome Black T as an indicator, the alkaline earth can be titrated with Na_2EDTA .

2.2 All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, because the color of the solution fades after standing. The optimum pH of the titration is 10.4 or above.

2.3 Additional information on the principle of the determination is given by Goetz and others (1950), and by Botha and Webb (1952).

3. Interferences

3.1 The salt Na_2EDTA also forms stable complexes with iron, manganese, copper, lead, cobalt, zinc, and nickel. Heavy-metal interferences can usually be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure can be used to analyze undiluted samples having iron, copper, zinc, or lead concentrations as high as 10 mg/L.

3.2 The higher oxidation states of manganese than manganese(II) react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent manganese interference can be removed by addition of one or two small crystals of potassium ferrocyanide.

3.3 In the presence of high aluminum concentrations, a characteristic effect will be observed as the end point is approached. The blue color that indicates the end point will appear and then, after short standing, will revert to red. The reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed.

4. Apparatus

Visual-titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others report better results by using a visual-titration assembly consisting of a motor-driven stirrer, 25-mL buret, white porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base, and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker.

5. Reagents

5.1 *Ammonium hydroxide, concentrated* (sp gr 0.900).

5.2 *Calcium standard solution*, 1.00 mL = 1.00 mg CaCO_3 : Suspend 1.000 g CaCO_3 , dried at 180°C for 1.0 h, in approx 600 mL demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.3 *Eriochrome Black T indicator solution*, 0.4 g/L: Dissolve 0.40 g Eriochrome Black T in 100 mL demineralized water and dilute to 1 L with 95-percent ethanol. This indicator is stable for at least 2 months. The Eastman Kodak Co. reagent has been found to be satisfactory.

5.4 *Hydroxylamine hydrochloride solution*, 30 g/L: Dissolve 30 g $\text{NH}_2\text{OH}\cdot\text{HCl}$ in demineralized water and dilute to 1 L.

5.5 *Potassium ferrocyanide*, crystals.

5.6 *Sodium cyanide solution*, **CAUTION: NaCN is a deadly poison, and the reagent solution must be so marked**, 2.5 g/100 mL: Dissolve 2.5 g NaCN in demineralized water and dilute to 100 mL.

5.7 *Na_2EDTA standard solution*, 1.00 mL = 1.00 mg CaCO_3 : Dissolve 3.72 g $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, dried overnight in a H_2SO_4 desiccator, in demineralized water and dilute to 1,000 mL. The reagent is stable for several weeks and a larger volume is usually prepared. Check the titer of the reagent by titrating 25.0 mL calcium standard solution as described in the procedure for sample analysis.

6. Procedure

6.1 Pipet a volume of sample containing less than 25 mg hardness (50.0 mL max) into a 150-mL beaker, and adjust the volume to approx 50 mL.

6.2 Insert the beaker in the titration assembly and start the stirrer.

6.3 Add 1 mL $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution.

6.4 Add 1 mL concentrated NH_4OH . (If not tightly stoppered, it tends to lose strength, and 1 mL of weak NH_4OH will not buffer the solution to the desired pH).

6.5 Add 2 mL NaCN solution--**CAUTION: deadly poison**. The addition of NaCN may be omitted if copper, zinc, lead, cobalt, and nickel are entirely absent, and if the sample contains less than 0.25 mg Fe and 0.025 mg Mn.

6.6 If manganese is present, add one or two small crystals of $\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$. Stir and wait at least 5 min until the $\text{Mn}_2\text{Fe}(\text{CN})_6$ precipitates.

6.7 Add 2.0 mL Eriochrome Black T indicator solution.

6.8 Titrate with Na_2EDTA standard solution until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared and the solution is clear blue. The change in color occurs rapidly; so the end point of the titration must be approached cautiously.

7. Calculations

Hardness,

$$\text{as CaCO}_3 \text{ (mg/L)} = \frac{1,000}{\text{ML sample}} \times \text{mL titrant}$$

8. Report

Report hardness, as CaCO₃ (00900), as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for hardness for 37 samples within the range of 3.2 to 312 mg/L may be expressed as follows:

$$S_T = 0.041X + 0.310$$

where

S_T = overall precision, milligrams per liter,
and

X = concentration of hardness, milligrams per liter as CaCO₃. The correlation coefficient is 0.8105.

9.2 Precision for hardness for six of the 31 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
14	3.22	90
11	4.50	7
8	50.5	3
14	105	3
8	232	3
11	312	4

References

- Botha, C. R., and Webb, M. M., 1952, The versenate method for the determination of calcium and magnesium in mineralized waters containing large concentrations of interfering ions: Institute of Water Engineers Journal, v. 6.
- Goetz, A., Loomis, T. C., and Diehl, H., 1950, Total hardness in water-the stability of standard disodium dihydrogen ethylenediamine tetraacetate solutions: Analytical Chemistry, v. 22, p. 798-9.