METHOD # 130.2	Approved for NPDES (Editorial Revision 1978, 1982)
TITLE:	Hardness, Total (mg/L as CaCO$_3$) (Titrimetric, EDTA)
ANALYTE:	Hardness Total (mg/L as CaCO$_3$)
INSTRUMENTATION:	Titration
STORET No.	00900

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg CaCO$_3$.

1.3 Automated titration may be used.

2.0 Summary of Method

2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na$_2$EDTA). The end point of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

3.0 Sample Handling and Preservation

3.1 Cool to 4°C, HNO$_3$ to pH < 2.

4.0 Comments

4.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.

    4.1.1 Routine addition of sodium cyanide solution (Caution: deadly poison) to prevent potential metallic interference is recommended.

5.0 Apparatus

5.1 Standard laboratory titrimetric equipment.

6.0 Reagents

6.1 Buffer solution

    6.1.1 If magnesium EDTA is available: Dissolve; 16.9 g NH$_4$Cl in 143 mLconc.

NH$_4$OH in a 250 mL volumetric, add 1.25 g of magnesium salt of EDTA and dilute to the mark with distilled water. Then go to 6.1.3.

6.1.2   If magnesium EDTA is unavailable: Dissolve 1.179 g disodium EDTA (analytical reagent grade) and 780 mg MgSO$_4$•7H$_2$O (or 644 mg MgCl$_2$•6H$_2$O) in 50 mL distilled water. Add this solution to a 250 mL volumetric flask containing 16.9 g NH$_4$Cl and 143 mL conc. NH$_4$OH with mixing and dilute to the mark with distilled water.

6.1.3   Store in a tightly stoppered plastic bottle; stable for approximately one month. Dispense with bulb operated pipet. Discard when 1 or 2 mL added to sample fails to produce a pH of 10.0 ± 0.1 at end point of titration.

6.1.4   Commercially available "odorless buffers" which are more stable, may be used.

6.2   Inhibitors: For most waters inhibitors are not necessary. If interfering ions are present use one of the following:

6.2.1   Inhibitor I: NaCN powder. (Caution: extremely poisonous). Flush solutions or sample containing this down drain using large quantities of water. Make sure no acids are present which might liberate HCN gas.

6.2.2   Inhibitor II: dissolve 5.0 g Na$_2$S•9H$_2$O or 3.7 g Na$_2$S•5H$_2$O in 100 mL distilled water. Exclude air with tightly fitted rubber stopper. This gives sulfide precipitates which may obscure the end point if large quantities of heavy metals are present. Deteriorates rapidly through air oxidation.

6.2.3   Inhibitor III: Dissolve 4.5 g hydroxylamine hydrochloride in 100mL of 95% ethanol or isopropanol.

6.3   Indicator: Use a commercially available indicator such as Calmagite indicator (Mallinckrodt) or one of the formulations described below (6.3.1-6.3.3):

6.3.1   Mix 0.5 g Eriochrome Black T with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 mL of 95% ethanol or isopropanol.

6.3.2   Dissolve 0.5 to 1.0 g Eriochrome Black T in an appropriate solvent such as triethanolamine or 2-methoxyethanol. Stable approximately one week.

6.3.3   Mix together 0.5 g Eriochrome Black T and 100 g NaCl.

6.4   Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, Na$_2$H$_2$C$_{10}$H$_{12}$O$_8$N$_2$•2H$_2$O in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (6.4.1) by titration (6.4.5). Store in polyethylene. Check periodically because of gradual deterioration.

6.4.1   Standard calcium solution 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in metals) in a 500 mL flask. Add, a little at a time, 1 + 1 HCl (6.4.2) until all of the CaCO$_3$ has dissolved. Add 200 mL distilled water. Boil for a few minutes to expel CO$_2$. Cool. Add a few drops of methyl red indicator (6.4.3) and adjust to intermediate orange color by adding 3N NH$_4$OH (6.4.4) or 1 + 1 HCl (6.4.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water

6.4.2   Hydrochloric acid solution, 1 + 1.

6.4.3   Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 mL volumetric flask and dilute to the mark.

6.4.4   Ammonium hydroxide solution, 3 N: Dilute 210 mL of conc. NH$_4$OH to

1 liter with distilled water.

6.4.5   Standardization titration procedure: Place 10.0 mL standard calcium solution (6.4.1) in vessel containing about 50 mL distilled water. Add 1 mL buffer solution (6.1). Add 1-2 drops indicator (6.3) or small scoop of dry indicator (6.3.3). Titrateslowly with continuous stirring until the last reddish tinge disappears, adding last few drops at 3-5 second intervals. At end point the color is blue. Total titration duration should be 5 minutes from the time of buffer addition

$$\text{N of EDTA} = \frac{0.2}{\text{mL of EDTA}}$$

6.5   Ammonium Hydroxide, 1 N: Dilute 70 mL of conc. NH_4OH to 1 liter withdistilled water.

7.0   Procedure

7.1   Pretreatment
7.1.1   For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.
7.1.2   For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2   Titration of sample-normal to high hardness:
7.2.1   Sample should require <15 mL EDTA titrant (6.4) and titration should be completed within 5 minutes of buffer addition.
7.2.2   Place 25.0 mL sample in titration vessels, neutralize with 1 N ammonium hydroxide (6. 5) and dilute to about 50 mL.
7.2.3   Add 1 to 2 mL buffer solution (6.1).
7.2.4   If end point is not sharp (as determined by practice run) add inhibitor at this point (see 7.4).
7.2.5   Add 1 to 2 drops indicator solution (6.3.1 or 6.3.2) or small scoop of dried powder indicator formulation (6.3.3).
7.2.6   Titrate slowly with continuous stirring with standard EDTA titrant (6.4) until last reddish tint disappears. Solution is normally blue at end point.

7.3   Titration of sample-low hardness (less than 5 mg/L)
7.3.1   Use a larger sample (100 mL)
7.3.2   Use proportionately larger amounts of buffer, inhibitor and indicator.
7.3.3   Use a microburet and run a blank using redistilled, distilled or deionized water.

7.4   To correct for interferences:
7.4.1   Some metal ions interfere by causing fading or indistinct end points. Inhibitors reduce this in accord with the scheme below for 25.0 mL samples diluted to 50 mL.

Maximum Concentrations of Interferences Permissible with Various Inhibitors[a]

Interfering Substance	Maximum Interference Concentration mg/L		
	Inhibitor I	Inhibitor II	Inhibitor III
Aluminum	20	20	20
Barium	b	b	b
Cadmium	b	20	b
Cobalt	over 20	0.3	0c
Copper	over 30	20	0.3
Iron	over 30	5	20
Lead	b	20	b
Manganese (Mn^{2+})	b	1	1
Nickel	over 20	0.3	0[c]
Strontium	b	b	b
Zinc	b	200	b
Polyphosphate		10	

(a) Based on 25-mL sample diluted to 50 mL.

(b) Titrates as hardness.

(c) Inhibitor fails if substance is present.

    7.4.2 Inhibitor I: At step 7.2.4 add 250 mg NaCN. Add sufficient buffer to achieve Ph 10.0 ± 0.1 to offset alkalinity resulting from hydrolysis of sodium cyanide.

    7.4.3 Inhibitor II: At step 7.2.4 add 1 mL of inhibitor II (6.2.2)

    7.4.4 Inhibitor III: At step 7.2.4 add 1 mL of inhibitor III (6.2.3).

8.0 Calculations:

$$\text{Hardness (EDTA) mg } CaCO_3/L = \frac{A \times N \times 50{,}000}{mL\ sample}$$

    Where:
    A = mL EDTA titrant (6.4)
    N = normality of EDTA titrant

9.0 Precision and Accuracy

    9.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

Increment as Total Hardness mg/liter, CaCO$_3$	Precision as Standard Deviation mg/liter, CaCO$_3$	Bias, %	Accuracy as Bias, mg/liter, CaCO$_3$
31	2.87	-0.87	-0.003
33	2.52	-0.73	-0.24
182	4.87	-0.19	-0.4
194	2.98	-1.04	-2.0
417	9.65	-3.35	-13.0
444	9.73	-3.23	-14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

9.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 194 mg CaCO$_3$, the standard deviation was± 3.

9.3 A synthetic unknown sample containing 610 mg/L total hardness as CaC0$_3$ contributed by 108 mg/L Ca and 82 mg/L Mg, and the following supplementary substances: 3.1 mg/L K, 19.9 mg/L Na, 241 mg/L chloride, 0.25 mg/L nitrite N, 1.1 mg/L nitrate N, 259 mg/L sulfate, and 42.5 mg/L total alkalinity (contributed by NaHCO$_3$) in distilled water wasanalyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8% .

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1126-67, p161, Method B (1976).