

Experiment 8

Determination of the Hardness of Natural Waters—

A: Conventional EDTA Complexometric Titration

B: Commercial Test Kit Determination

Objectives—The objectives of this experiment are:

1. To measure the hardness of environmental waters from several sites to determine the effect of location on hardness
2. To show how hardness may be readily measured in the field using a test kit.

Introduction—The hardness of water was originally defined in terms of its ability to precipitate soap. Calcium and magnesium ions are the principal causes of hardness in water, although iron, aluminum, manganese, strontium, zinc, and hydrogen ions are also capable of producing the same effect. The total hardness of water is now defined as the amount of calcium and magnesium present and is expressed as ppm calcium carbonate.

The procedure for determining both calcium and magnesium, when present together, is found in many schemes of applied analysis, including the analysis of minerals, blood serum, and food, and is the standard method for determining water hardness.

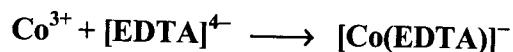
The hardness test is one of the most commonly performed analyses in the water industry. High levels of hardness are undesirable and must be removed before the water is used by the beverage, laundry, metal-finishing, dyeing and textiles, food, and paper pulp industries. Hardness levels greater than 500 ppm calcium carbonate are undesirable for domestic use and most drinking water supplies average about 250 ppm. Table 8-1 lists the various classes of hardness.

Table 8-1 Classes of Hardness Based on Hardness Range

HARDNESS RANGE (ppm CaCO ₃)	HARDNESS DESCRIPTION
0–50	Soft
51–150	Moderately Hard
151–300	Hard
>300	Very Hard

Source: G. Tchobanoglous and E. D. Schroeder, *Water Quality*, Addison-Wesley, Reading, MA, 1985.

Theory—Metal ions act as Lewis acids. Anions or molecules with unshared pairs of electrons can act as Lewis bases and covalently bind to metal ions. The electron-pair donors are called ligands, and the species formed in the reaction are known as complex ions if ionic or complexes (or coordination compounds) if neutral. Ligands that bind to the metal at more than one coordination site are called polydentate. The ethylenediaminetetraacetate ion, abbreviated EDTA, is an important polydentate ligand. This species has six donor atoms and is thus hexadentate. It reacts with many metal ions in a 1:1 ratio to form very stable complexes, as in the equation:



EDTA is a tetraprotic acid and is frequently represented as H_4Y . The usual form of EDTA is the disodium salt, $\text{Na}_2\text{H}_2\text{Y}$. When this form is used as the titrant in a complexometric titration, the titration reaction is:



Since hydronium ion is produced, a buffer is necessary since calcium and magnesium ions must be titrated at high pH for stable complexes to be formed and for the proper functioning of the indicator.

The indicators used for EDTA titrations are called metallochromic indicators, and for the most part they are weakly acidic organic dyes. They include Eriochrome Black T (Erio T or EBT), the first one discovered, Calcon, and Calmagite. EBT functions by forming a colored metal complex, MEBT^- , at the start of the titration. As long as some metal remains unchelated by EDTA, the solution being titrated remains the color of the MEBT^- complex. At the equivalence point, EDTA removes the metal ion from the indicator-metal complex by chelating it, and the solution changes color:



Titrant	color I before end point	color II at end point
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The hardness due to calcium and magnesium ions separately can be determined by using the fact that at very high pH, magnesium forms the insoluble hydroxide, $\text{Mg}(\text{OH})_2$, whereas calcium remains in solution. The calcium can then be titrated with standard EDTA and its concentration determined. If another sample is titrated with EDTA at a lower pH, both calcium and magnesium ions react. The magnesium hardness is found by the difference in titrant volume used for the two samples.

Some ions, notably iron(III), block the indicator by combining irreversibly with it. In this case the interfering ion must either be removed or chemically tied up before titrating with EDTA.

It is frequently necessary to obtain a quick analysis of a particular chemical on-site. Many test kits have been developed for analysis "in the field." These test kits offer simplicity and portability, in exchange for accuracy and precision. The analysis of well water is often performed to determine whether a water softener would improve water quality.

Safety Issues

1. Safety glasses must be worn at all times in the laboratory and when testing samples in the field.
2. The authors have not had any difficulty with iron masking the indicator. However, if iron concentrations are high enough, an iron precipitate will form that will also interfere in a hardness measurement unless it is filtered.

Procedure

A: Conventional Titrimetry

1. Prepare a standard solution of EDTA by dissolving about 0.9 g (weighed to 0.1 mg) of certified ACS grade Na_2EDTA in enough water to give 250 mL of solution, using a volumetric flask. (For more accuracy, the EDTA can be standardized by titrating samples of primary standard calcium carbonate dissolved in acid, to which a very small amount of magnesium ion is added for the indicator to function properly.)
2. Pipet 10.00 mL of filtered river water sample into a 250 mL Erlenmeyer flask, and dilute to about 50 mL with DI water. Add 15 mL of pH 10 buffer (provided) and mix thoroughly. Add 4 drops of EBT indicator (see Note 2) and titrate with standard 0.01 M EDTA until a pure blue color, with no tinge of purple, is obtained. Repeat this procedure for two additional samples, increasing the volume of sample if not more than 10 mL of titrant is used for the analysis (see Note 3).
3. Repeat Step 2 (triplicate analysis) for another sample type. This sample can be tap water, or any other sample of interest (see Note 3).

B: Using a HACH Test Kit

1. Fill the plastic measuring tube to the top (level) with the water to be tested, and transfer it to the square mixing bottle.
2. Add the contents of one UniVer III Hardness Reagent Powder Pillow, using the clipper to open. Swirl to mix.
3. While swirling the sample and counting drops, add the Titrant Reagent (Hardness 3) dropwise until the color changes from red to blue in one drop.
4. The hardness of the water in grains per gallon, expressed as calcium carbonate, is the number of drops of Titrant Reagent (Hardness 3) used (1 grain = 64.8 mg and 1 gal = 3.7854 L).
5. To convert the result from grains CaCO_3 per gallon to mg/L (ppm), multiply the number of drops from Step 3 by 17.1.

Waste Reduction and Disposal

1. Water samples from previous experiments can be used for this experiment. Tap water and bottled water samples can be disposed of by flushing down the laboratory drain. Your instructor will advise you on the disposal of any environmental water samples that may be considered to be hazardous wastes.
2. Any extra solid EDTA taken should be placed in a designated bottle and not returned to the original stock bottle. Any extra EDTA titrant and the products of the titrations can be disposed of in the laboratory drain (if your instructor indicates that this is acceptable practice).
3. There should not be any waste pH 10 buffer, but if there is it can be disposed of in the laboratory drain (again, your instructor will give specific instructions on disposal policy).

Data Analysis

1. Report the concentration of the standard EDTA.
2. Report the total hardness, in ppm CaCO_3 , for each determination. Since mol EDTA = mol metal from the titration reaction, the moles of calcium carbonate are equal to the moles of EDTA used in a titration. This is finally converted into mg CaCO_3/L of sample.
3. Report the mean and median values for each type of sample analyzed.
4. Report the range and the relative standard deviation for each type of sample analyzed in triplicate. Discuss the precision and compare with results obtained in other experiments, such as the determination of chloride.
5. **Compare the two methods.** Compare concentrations obtained using the standard EDTA method with the result using a commercial kit. Discuss the difference, if any.
6. Compare your hardness results with those given in Table 8-1 and classify the hardness of your samples accordingly. Table 8-2 shows hardness results in the authors' area that you can use for comparison.

Table 8-2 Results of Hardness Analyses for Previous Years in the Authors' Area

Average hardness of St. Johns River Water	1882 ppm CaCO_3
Average range of hardness for St. Johns River Water	18 ppm CaCO_3
Average hardness of lab tap water	303 ppm CaCO_3

Supplemental Activity

1. Compare your hardness results with the hardness of seawater. Seawater itself is a good sample to study.
2. If time permits, also determine the hardness of bottled spring water.

Questions and Further Thoughts

1. Could a conductometric titration be used to determine the end point in a complexometric titration, like the one studied in this experiment?
2. Show that the conversion factor for grains calcium carbonate/gal to ppm calcium carbonate is 17.1.

Notes

1. Calcon and some other metallochromic indicators can be used in solid form.
2. Do not use an EBT solution that is older than 2 weeks. Indicator labels should have a date.
3. If the concentration of iron is small, it will form hydroxo complexes that will not interfere with the indicator. If the iron concentration is high, it will precipitate out in the pH 10 buffer. In precipitated form it will still mask the EBT and should be filtered.

Literature Cited

1. A. E. Greenberg, L. S. Clesceri, and A. D. Eaton, Eds., *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, DC, 1992.
2. D. A. Skoog, D. M. West, and F. J. Holler, *Fundamentals of Analytical Chemistry*, 7th ed., Saunders, New York, 1996.
3. G. Tchobanoglous and E. D. Schroeder, *Water Quality*, Addison-Wesley, Reading, MA, 1985.