

DETERMINATION OF HARDNESS IN A WATER SAMPLE

Purpose: To learn the EDTA titration method for determining the hardness of a water sample

BACKGROUND

In the past, *water hardness* was defined as a measure of the capacity of water to precipitate soap. However, current laboratory practices define total hardness as the sum of divalent ion concentrations, especially those of calcium and magnesium, expressed in terms of mg CaCO_3/L . There are no known adverse health effects of hard or soft water, but the presence of hard waters results in two economic considerations: (1) hard waters require considerably larger amounts of soap to foam and clean materials, and (2) hard waters readily precipitate carbonates (known as *scale*) in piping systems at high temperatures. Calcium and magnesium carbonates are two of the few common salts whose solubility decreases with increasing temperature. This is due to the removal of dissolved CO_2 as temperature increases. The advent of synthetic detergents has significantly reduced the problems associated with hard water and the “lack of foaming.” However, scale formation continues to be a problem.

The source of a water sample usually determines its hardness. For example, surface waters usually contain less hardness than do groundwaters. The hardness of water reflects the geology of its source. A color-coded summary of water hardness in the United States can be found at <http://www.usgs.org>, and if

TABLE 22-1. Correlation of Water Hardness Values with Degrees of Hardness

mg CaCO ₃ /L Hardness	Degree of Hardness
0–75	Soft
75–150	Moderately hard
150–300	Hard
>300	Very hard

you view this map you will see that hardness values can range from less than 50 mg/L to over 250 mg/L. Therefore, depending on your water's source, some modifications to the procedure described below may be necessary. Carbonates in surface soils and sediments increase the hardness of surface waters, and subsurface limestone formations also increase the hardness of groundwaters. As indicated in Table 22-1, hardness values can range from a few to hundreds of milligrams of CaCO₃ per liter.

The divalent metal cations responsible for hardness can react with soap to form precipitates, or when the appropriate anions are present, to form scale in hot-water pipes. The major hardness-causing cations are calcium and magnesium, although strontium, ferrous iron, and manganese can also contribute. It is common to compare the alkalinity values of a water sample to the hardness values, with both expressed in mg CaCO₃/L. When the hardness value is greater than the total alkalinity, the amount of hardness that is equal to the alkalinity is referred to as the *carbonate hardness*. The amount in excess is referred to as the *noncarbonate hardness*. When the hardness is equal to or less than the total alkalinity, all hardness is carbonate hardness and no noncarbonate hardness is present. Common cations and their associated anions are shown in Table 22-2.

THEORY

The method described below relies on the competitive complexation of divalent metal ions by ethylenediaminetetraacetic acid (EDTA) or an indicator. The

TABLE 22-2. Common Cation–Anion Associations Affecting Hardness and Alkalinity

Cations Yielding Hardness	Associated Anions
Ca ²⁺	HCO ₃ [–]
Mg ²⁺	SO ₄ ^{2–}
Sr ²⁺	Cl [–]
Fe ²⁺	NO ₃ [–]
Mn ²⁺	SiO ₃ ^{2–}

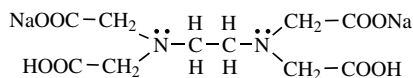


Figure 22-1. Chemical structure for the disodium salt of EDTA.

chemical structure for the disodium salt of EDTA is shown in Figure 22-1. Note the lone pairs of electrons on the two nitrogens. These, combined with the dissociated carboxyl groups, create a 1 : 1 hexadentate complex with each divalent ion in solution. However, the complexation constant is a function of pH (Harris, 1999). Virtually all common divalent ions will be complexed at pH values greater than 10, the pH used in this titration experiment and in most hardness tests. Thus, the value reported for hardness includes all divalent ions in a water sample.

Three indicators are commonly used in EDTA titration, Eriochrome Black T (Erio T), Calcon, and Calmagite. The use of Eriochrome Black T requires that a small amount of Mg^{2+} ion be present at the beginning of the titration. Calmagite is used in this experiment because its endpoint is sharper than that of Eriochrome Black T.

REFERENCES

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- Harris, D. C., *Quantitative Chemical Analysis*, 5th ed., W.H. Freeman and Company, New York, 1998.
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- Sawyer, C. N. and P. L. McCarty, *Chemistry for Environmental Engineering*, 3rd ed., McGraw-Hill, New York, 1978.
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IN THE LABORATORY

Two methods are available for determining the hardness of a water sample. The method described and used here is based on a titration method using a chelating agent. The basis for this technique is that at specific pH values, EDTA binds with divalent cations to form a strong complex. Thus, by titrating a sample of known volume with a standardized (known) solution of EDTA, you can measure the amount of divalent metals in solution. The endpoint of the titration is observed using a colorimetric indicator, in our case Calmagite. When a small amount of indicator is added to a solution containing hardness (at pH 10.0), it combines with a few of the hardness ions and forms a weak wine red complex. During the titration, EDTA complexes more and more of the hardness ions until it has complexed all of the free ions and “outcompetes” the weaker indicator complex for hardness ions. At this point, the indicator returns to its uncomplexed color (blue for Calmagite), indicating the endpoint of the titration, where only EDTA-complexed hardness ions are present.

Safety Precautions

- As in all laboratory exercises, safety glasses must be worn at all times.
- Avoid skin and eye contact with pH 10 buffer. In case of skin contact, rinse the area for several minutes. For eye contact, flush eyes with water and seek immediate medical advice.

Chemicals and Solutions

Sample Handling. Plastic or glass sample containers can be used. A minimum of 100 mL is needed, but for replicate analysis of low-hardness water, 1 L of sample is suggested. If you are titrating the sample on the day of collection, no preservation is needed. If longer holding times are anticipated, the sample can be preserved by adding nitric or sulfuric acid to a pH value of less than 2.0. Note that this acidic pH level must be adjusted to above a pH value of 10 before the titration.

- *pH 10 buffer.* In a 250-mL volumetric flask, add 140 mL of a 28% by weight NH_3 solution to 17.5 g of NH_4Cl and dilute to the mark.
- *Calmagite* [1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid]. Dissolve 0.10 g of Calmagite in 100 mL of distilled or deionized water. Use about 1 mL per 50-mL sample to be titrated.
- *Analytical reagent-grade Na_2EDTA* (FW 372.25). Dry at 80°C for 1 hour and cool in a desiccator. Accurately weigh 3.723 g (or a mass accurate to 0.001 g), dissolve in 500 mL of deionized water with heating, cool to room

temperature, quantitatively transfer to a 1-L volumetric flask, and fill to the mark. Since EDTA will extract hardness-producing cations out of most glass containers, store the EDTA solution in a plastic container. This procedure produces a 0.0100 *M* solution.

Glassware

- Standard laboratory glassware: 50-mL buret, 250-mL Erlenmeyer flasks, 50-mL beakers, Pasteur pipets

PROCEDURE

Limits of the Method. Detection limits depend on the volume of sample titrated.

1. Pipet an aliquot of your sample into a 250-mL Erlenmeyer flask. The initial titration will only be a trial and you will probably need to adjust your sample volume to obtain the maximum precision from your pipetting technique (use more than 10 mL but less than 50 mL). Increase or decrease your sample size as needed.
2. Add 3 mL of the pH 10 buffer solution and about 1 mL of the Calmagite indicator. Check to ensure that the pH of your sample is at or above pH 10. Add additional buffer solution if needed.
3. Titrate with EDTA solution and note the color change as you reach the endpoint. Continue adding EDTA until you obtain a stable blue color with no reddish tinge (incandescent light can produce a reddish tinge at and past the endpoint).
4. Repeat until you have at least three titrations that are in close agreement.
5. Calculate the hardness for each of your samples. Express your results in mg CaCO_3/L . If you made the EDTA solution exactly according to the procedure, 1.00 mL of EDTA solution is equal to 1.00 mg CaCO_3/L . Confirm this through calculations.

Waste Disposal

After neutralization, all solutions can be disposed of down the drain with rinsing.

ADVANCED STUDY ASSIGNMENT

1. In your own words, define *hardness*.
2. What are the primary cations typically responsible for hardness?
3. In what unit of measure is hardness usually expressed?
4. What is meant by *carbonate* and *noncarbonate hardness*?
5. What is the color change for the Calmagite indicator?
6. Briefly outline a procedure for titrating a water sample for hardness. (List the major steps.)
7. If you titrate 50.0 mL of a sample with 0.100 M EDTA and the titration takes 25.75 mL of EDTA to reach the endpoint, what is the hardness of the sample in mg CaCO_3/L ?