

## HARDNESS

Water that contains salts of calcium and magnesium and, to a lesser extent, other polyvalent metals, such as iron, aluminum, and manganese, and that requires large amounts of soap to lather or that, on evaporation, forms a deposit on the container is referred to as hard water. In early methodology, hardness was measured as the capacity of water to precipitate soap when a liquid soap solution was shaken with the water sample to form a lather persisting for 5 minutes. Hardness is now best defined as a characteristic of water representing the total concentration of calcium and magnesium ions expressed as milligrams of  $\text{CaCO}_3$  per liter. When other ions are present in insignificant amounts, the hardness will be equal to or less than the sum of the carbonate and bicarbonate alkalities and is termed *carbonate hardness*. If the hardness exceeds the sum of these alkalities, the presence of other ions is indicated, and the excess is expressed as *noncarbonate hardness*. Hardness determination is thus corroboratory to the findings of alkalinity; however, when used in conjunction with calcium determinations, it allows for the calculation of magnesium concentration, circumventing the laboratory analysis for this ion. Hard water is not generally considered harmful to man (except as a possible cause of kidney stones); within limitations, the ions present are necessary for normal plant and animal survival and growth. Evidence suggests that hardness may affect tolerance of fishes to toxic metals.

What actually constitutes "hard water" has been variously described. One reasonable classification is that by Brown, Skougstad, and Fishman (1970) for hardness as mg per liter  $\text{CaCO}_3$  and is as follows: 0 to 60 = soft, 61 to 120 = moderately hard, 121 to 180 = hard, and 181 and above = very hard.

The Eriochrome Black T indicator used in this titration produces a red color in the presence of calcium and magnesium ions. The disodium salt of EDTA forms a stable, colorless complex with these ions, effectively removing them from solution. Thus by titration of the sample containing the indicator with EDTA, the calcium and magnesium ions are quantitatively removed. When all ions are removed, the indicator changes to a bright blue color.

### Apparatus

Titration glassware  
Magnetic stirrer if available  
Daylight light source

### Reagents

*Buffer solution.* Use commercially prepared buffer as directed, or prepare per instructions in *Standard Methods*.

*Indicator.* Mix 0.8 g Eriochrome Black T dye and 100 g NaCl to prepare a dry powder mixture. ~~0.001M~~

*Standard EDTA titrant, ~~0.001M~~.* Dissolve 0.3723 g  $\text{Na}_2\text{EDTA}$ -dihydrate in distilled water and dilute to 100 ml. Check by titrating against a standard calcium solution: 1.00 ml = 1.00 mg  $\text{CaCO}_3$  = ~~0.4008 mg Ca~~. *0.04008 mg Ca*

*Standard calcium solution.* Weigh 1.000 g anhydrous calcium carbonate powder, primary standard grade, into a 500 ml Erlenmeyer flask. Add slowly one volume HCl diluted with an equal volume of distilled water (1 + 1 HCl) until all the  $\text{CaCO}_3$  has dissolved. Add 200 ml distilled water, and boil for a few minutes to expel  $\text{CO}_2$ . Cool, and adjust to pH 5.0 with either  $\text{NH}_4\text{OH}$  (about 3 N) or 1 + 1 HCl. Transfer to a 1-liter volumetric flask, washing out the Erlenmeyer flask several times with distilled water and adding to volumetric flask. Then dilute to mark with distilled water. (1.00 ml = 1.00 mg  $\text{CaCO}_3$  = 0.4008 mg Ca.)

### Procedure

1. Dilute 25 ml of sample to about 50 ml with distilled water in titration flask.
2. Add 1 to 2 ml of buffer solution to bring pH to 10.0 or 10.1.
3. Add approximately 0.1 g indicator powder (just a bit on the tip of a spoon or spatula).
4. Titrate with EDTA over a white surface with daylight or white light. Stir continuously until the last red tinge disappears. Add the last drops slowly, allowing about 5 seconds between drops. The entire duration of titration should not exceed 5 minutes and should not require more than 15 ml of titrant. If more titrant than this is used, take a smaller aliquot and repeat titration. An indistinct end point suggests interference and calls for an inhibitor after step 2. Faulty (old) indicator powder also produces an indistinct end point.

optional