

## Hardness

Water hardness was once considered to be a measurement of a water sample's capacity to precipitate soap. However, in current practice, the total hardness is defined as the sum of the concentrations of calcium and magnesium; expressed in terms of mg  $\text{CaCO}_3/\text{L}$ . There are no known adverse health effects of consuming relatively hard or soft water, but the presence of hard waters results in two economically noteworthy details: (1) hard waters require considerable 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. The advent of synthetic detergents has significantly reduced problems associated with hard water and its inability to effectively wash with soaps. However, scale formation continues to be a problem.

The source of a water sample usually determines its hardness. For example, surface waters commonly contain less hardness than ground waters. The hardness of the water is reflected by the geological formations from where the water is derived. Carbonates naturally present in surface soils and sediments will increase the hardness of surface waters. Similarly, subsurface limestone formations increase the hardness of subsurface waters. Hardness values may range from a few to hundreds of mg  $\text{CaCO}_3/\text{L}$ .

Hardness is the result of divalent metal cations. These metal ions are capable of reacting with soap to form precipitates, or, in the presence of the appropriate anions, scale may form in hot water pipes. The major hardness-causing cations are calcium and magnesium though strontium, ferrous iron, and manganese may also contribute to hardness. It is common to compare the alkalinity values of a water to the values of its hardness, both of which are expressed in terms of mg  $\text{CaCO}_3/\text{L}$ . In the case that 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" while the excess amount of hardness is referred to as the "noncarbonate hardness". On the other hand, when the hardness is equal to or less than the total alkalinity, all hardness is carbonate hardness and there will be no noncarbonate hardness present.

There are two methods used in determining the hardness of a water. The one described and used here in this procedure is based on a titration method making use of a chelating agent. The basis for this technique is that at specific pH values, ethylenediaminetetraacetic acid (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, one can measure the amount of divalent metals in solution. The titration's endpoint is observed using a colorimetric indicator, Eriochrome Black T. When a small amount of Eriochrome Black T (blue in color while in the absence of divalent metals) is added to a solution containing hardness (at pH = 10.0), it combines with a few of the hardness ions to form a weak wine red complex. During the titration with EDTA, more and more of the hardness ions are complexed with EDTA. Eventually, there is a point at which the EDTA has complexed all of the free ions and "out-competes" the weaker Eriochrome Black T complex for hardness ions. At this point, the Eriochrome Black T returns to its uncomplexed blue color, indicating that only EDTA-complexed hardness ions are present in the endpoint of the titration.

References:

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