Course Number : CE 332
Course Name : Environmental Engineering Lab
Course Credit : 1.50

Experiment No. 7
Determination of Hardness of Water

BACKGROUND

Hard waters are generally considered to be those waters that require considerable amounts of soap to produce a foam or lather and that also produce scale in hot-water pipes, heaters, boilers, and other units in which the temperature of water is increased substantially. The hardness of water varies considerably from place to place. In general, surface water is softer than groundwater. The hardness of water reflects the nature of the geological formations with which it has been in contact.

Hardness is caused by multivalent metallic cations. Such cations are capable of reacting with soap to form precipitates and with certain anions present in water to form scale. The principal hardness causing cations are the divalent calcium, magnesium, strontium, ferrous iron, and manganous ions. These cations and the important anions with they are associated are shown in Table 1 in the order of their relative abundance in natural waters. Aluminum and ferric ions are sometimes considered as contributing to the hardness of water. However, their solubility is so limited at pH values of natural waters that ionic concentrations are negligible. The hardness of water is derived largely from contact with the soil and rock formations.

Table 1. Principal cations causing hardness and the major anions associated with them

Cations causing Hardness	Anion
Ca^{2+}	HCO_3^-
Mg^{2+}	SO_4^{2-}
Sr^{2+}	Cl^-
Fe^{2+}	NO_3^-
Mn^{2+}	SiO_3^{2-}

ENVIRONMENTAL SIGNIFICANCE

Hard waters are as satisfactory for human consumption as soft waters. Because of their adverse action with soap, however, their use for cleansing purpose is quite unsatisfactory, unless soap costs are disregarded. Soap consumption by hard waters represents an economic loss to the water user. Sodium soaps react with multivalent metallic cations to form a precipitate, thereby losing their surfactant properties. In recent years these problems have been largely alleviated by the development of soaps and detergents that do not react with hardness.

Boiler scale, the result of the carbonate hardness precipitation, may cause considerable economic loss through fouling of water heater and hot water pipes. Changes in pH in the water distribution systems may also result in deposits of precipitates. Bicarbonates begin to convert to the less soluble carbonates at pH values above 9.0.

Magnesium hardness, particularly associated with the sulfate ion has a laxative effect on persons unaccustomed to it. Magnesium concentrations of less than 50 mg/l are desirable in potable waters, although many public water supplies exceed the amount. Calcium hardness presents no public health problem. In fact, hard water is apparently beneficial to the human cardiovascular system.

Water are generally classified in terms of the degree of hardness as follows:

Soft	<50 mg/l as $CaCO_3$
Moderately hard	50 - 150 mg/l as $CaCO_3$
Hard	150 - 300 mg/l as $CaCO_3$
Very hard	> 300 mg/l as $CaCO_3$

THEORY

Hardness is usually expressed in terms of $CaCO_3$. Perhaps the most accurate method of determining hardness is by a calculation based upon the divalent ions found through complete cation analysis. This method is preferred where complete analyses are available. Hardness caused by each cation can be calculated as follows:

$$\text{Hardness (as mg/l } CaCO_3) = M^{2+} \text{ (mg/l)} \times 50 / (\text{Equivalent weight of } M^{2+}) \quad (1)$$

where, M^{2+} = concentration of divalent metal cation in mg/l and 50 is the equivalent weight of $CaCO_3$.

However, complete analyses of metal ions are not always available and in laboratory total hardness is usually determined by the ***EDTA Titrimetric Method***. This method yields very precise and accurate results and is the method of choice in most laboratories.

The EDTA Titrimetric method involves the use of solutions of (ethylene-diamine-tetra acetic acid) (EDTA) or its sodium salt as the titrating agent. These compounds are chelating agents and form extremely stable complexes with Ca^{2+}, Mg^{2+} and other divalent cations causing hardness, as shown in Eq. 2.

$$M^{2+} + EDTA = [M.EDTA]_{complex} \quad (2)$$

The successful use of EDTA for determining hardness depends upon having an indicator present to show when EDTA is present in excess, or when all the ions causing hardness have been complexed.

The Eriochrome Black T dye serves as an excellent indicator to show when all the hardness ions have been complexed. When a small amount of Eriochrome Black T, having a blue color, is added to hard water with a pH of about 10.0, it combines with a few of the Ca^{2+} and Mg^{2+} ions to form a weak complex ion which is wine red in colour (Eq. 3).

$$M^{2+} + \text{Eriochrome Black T} = (\text{M.Eriochrome Black T})_{complex} \quad (3)$$
$$\text{(wine red colour)}$$

During titration with EDTA, all free hardness ions are complexed according to Eq. 2. Finally, the EDTA disrupts the wine red (M.Eriochrome Black T) because it is capable of forming more stable complex with the hardness ions. This action frees the Eriochrome Black T indicator, and the wine red color changes to a distinct blue colour (Eq. 4), indicating the end of titration.

(M.Eriochrome Black T) $_{complex}$ + EDTA(M.EDTA)conipiex + Eriochrome Black T (4)
(wine red color) (blue color)

REAGENTS:

(1) Buffer solution (for attaining a pH close to 10.0).
(2) Eriochrome Black T dye.
(3) Standard EDTA solution.

(Note: The above three reagents have been procured from HACT Co., USA)

APPARATUS

1. Beaker	: 1 pc
2. Measuring cylinder	: 1 pc
3. Dropper	: 1 pc
4. Srirrer	: 1 pc
5. HACH auto-titration device	: 1 set

PROCEDURE

(1) Take 50 ml sample in a 150 ml beaker.
(2) Add one ml of standard buffer solution (supplied by HACH) to raise the pH of water sample to about 10.0 (Note: If 100 ml sample is taken, add 2 ml buffer).
(3) Add one packet of Eriochrome Black I dye (supplied by HACH) indicator to the beaker. The sample would turn wine-red (if hardness is present).
(4) Fit the cartridge containing standard EDTA solution to the titrator device (supplied by HACH).
(5) Turn the flow control knob of the device until the solution starts to come out of the tube fitted to the cartridge. Take initial reading of the counter.
(6) Immerse the tube fitted to the cartridge into the water sample and start titrating (under constant stirring) by turning the flow control knob of the auto-titrator. Continue until the wine-red color of the sample changes to blue. Take final reading of the counter.

CALCULATION

Total hardness as mg/l $CaCO_3$ = 2 × (initial counter reading - final counter reading)

If 100 ml sample is taken, hardness = (initial counter reading - final counter reading)

TYPES OF HARDNESS

In addition to total hardness, it is often desirable and sometimes necessary to know the type of hardness present. Hardness is classified in two ways: (1) with respect to the metallic ion (calcium and magnesium

hardness), and (2) with respect to the anions associated with the metallic ions (carbonate and non-carbonate hardness).

Calcium and Magnesium Hardness

Calcium and magnesium cause by far the greatest portion of the hardness occurring in natural waters. Sometimes, it is important to know the amounts of calcium and magnesium hardness in water. For example, it is necessary to know the magnesium hardness or the amount of Mg> in order to calculate lime requirement in lime-soda ash softening. The calcium and magnesium hardness may be calculated from the complete chemical analysis. If calcium hardness is determined, magnesium hardness is obtained by subtracting calcium hardness from total hardness as follows:

Total hardness - calcium hardness = magnesium hardness (5)

Carbonate and Non-carbonate Hardness

The part of total hardness that is chemically equivalent to the bicarbonate plus carbonate alkalinities present in water is considered to be ***carbonate hardness***. Since alkalinity and hardness are both expressed in terms of $CaCO_3$, the carbonate hardness can be found as follows:

When alkalinity < total hardness,
Carbonate hardness (mg/l) = alkalinity (mg/l) (6)

When alkalinity ≥ total hardness,
Carbonate hardness (mg/l) = total hardness (mg/l) (7)

Carbonate hardness is of particular interest because the bicarbonate and carbonate ions with which it is associated tend to precipitate this portion of the hardness at elevated temperatures such as occur in boilers or during the softening process with lime. Carbonate hardness was formerly called ***temporary hardness*** because it can be caused to precipitate by prolonged boiling (Eq. 8).

$$Ca^{2+} + 2HCO_3 = CaCO_3\,(s) + CO_2 + H_2O \quad (8)$$
$$Ca^{2+} + 2HCO_3 + Ca(OH)_2 = 2CaCO_3\,(s) + 2H_2O \quad (9)$$

The amount of hardness which is in excess of the carbonate hardness is called *noncarbonate hardness*, and can be estimated as follows:

Non-carbonate hardness (NCH) = total hardness - carbonate hardness (10)

Non-carbonate hardness was formerly called *permanent hardness* because it cannot be removed or precipitated by boiling. Non-carbonate hardness cations are associated with sulfate, chloride, and nitrate anions.

Pseudo-Hardness

Sea, brackish, and other waters that contain appreciable amounts of Na^+ interfere with the normal behavior of soap because of the common ion effect. Sodium is not a hardness-causing cation, and so this action which it exhibits when present in water in high concentration is termed *pseudo-hardness*.

ASSIGNMENT QUESTIONS

(1) What is hardness and how it is caused? Discuss the environmental significance of hardness.

(2) A water sample has the following analysis:

Na^+	20 mg/l	Cl^-	40 mg/l
Ca^{2+}	30 mg/l	HCO_3^-	67 mg/l
Mg^{2+}	10 mg/l	CO_3^{2-}	0 mg/l
Sr^{2+}	2 mg/l	SO_4^{2-}	5 mg/l
K^+	30 mg/l	NO^-	10 mg/l

What is the total hardness, carbonate hardness, and non-carbonate hardness in mg/l as $CaCO_3$?

(3) What do you understand by temporary hardness? A water sample has a total alkalinity of 265 mg/l and a total harness of 315 mg/l as $CaCO_3$. Calculate carbonate and non-carbonate hardness (in mg/l as $CaCO_3$) of the sample.