Experiment 7
Determination of Hardness in Water



Introduction:

Hard waters are generally considered to be those waters that require considerable amounts of soap to produce foam or leather and that also produce scale in hot-water pipes, 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 ion and manganaous ions.These cations and the important anions with they are associated with are shown in the following table 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 7.1: Principal hardness causing cations and the major anions associated with them

Cations causing Hardness	Associated Anions
Ca^{2+}	HCO_3^-
Mg^{2+}	SO_4^{2-}
Sr^{2+}	Cl^-
Fe^{2+}	NO^{3-}
Mn^{2+}	SiO_3^{2-}

Hardness caused by each cation can be calculated as follows:

$$\text{Hardness (mg/l as } CaCO_3) = \frac{M^{2+}(mg/l)\times 50}{Equivalent\ weight\ of\ M^{2+}} \qquad 7.1$$

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

$$\text{Total hardness} = \sum \left[\frac{50}{20.04} Ca^{2+} + \frac{50}{12.15} Mg^{2+} + \frac{50}{27.92} Fe^{2+} + \frac{50}{27.46} Mn^{2+}\right] \qquad 7.2$$

$$= \sum \left[2.49\ Ca^{2+} + 4.12\ Mg^{2+} + 1.79\ Fe^{2+} + \frac{50}{27.46} Mn^{2+}\right] \qquad 7.3$$

Environmental significance:

Hard water is as satisfactory for human consumption as soft water. Because of their action with soap, however, their use for cleansing purposes is quite unsatisfactory, unless soap costs are disregarded. Soap consumption by hard water 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. Change 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 can be generally classified in terms of the degree of hardness as follows:

Table 7.2: Water quality with respect to hardness

Water Quality	**Hardness (mg/l as $CaCO_3$)**
Soft	<50
Moderately hard	50-150
Hard	150-300
Very hard	>300

Theory on Experimental Method

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 the complete cation analysis (Equation 7.1 – 7.3). This method is preferred where complete analysis are available.

However, complete analysis of metal ions is 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 methods of choice in most laboratories.

The EDTA titrimetric method involves the use of solutions of ethylene-diamine-tetra-acidic acid (EDTA) or its sodium salt as the titrating agents. These compounds are chelating agents (A chemical compound in the form of a heterocyclic ring, containing a metal ion attached by coordinate bonds to at least two non-metal ions) and thus form extremely stable complexes with Ca^{2+}, Mg^{2+} and other divalent cations causing hardens, as shown in the following equation.

$$M^{2+} + EDTA = [M.EDTA]_{complex} \quad 7.4$$

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 Erichome Black T dye serves as an excellent indicator to show when all the hardness ions having form complex with EDTA. When small amount of Erichrome Black T 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 ions which produce wine red color in the solution.

$$M^{2+} + \text{Erichrome Black T} = (\text{M. Erichrome Black T})_{complex} \quad 7.5$$

During titration with EDTA, all free hardness ions are complexed according to euqtion7.2. Finally, the EDTA disrupts the weak wine red complex compounds (M. Erichrome Black T) and forms more stable complex with the divalent ions. The action frees the Erichrome Black T indicator, and the wine red colour changes to a distinct blue colour.

$$(\text{M. Erichrome Black T})_{complex} + EDTA = (\text{M. EDTA})_{complex} + \text{Erichrome Black T}_{(blue\ color)} \quad 7.6$$

Reagents:

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

Apparatus:

1. Beaker
2. Measuring cylinder
3. Dropper
4. Stirrer
5. Auto-titration device

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 the water sample to about 10.0.
3. Add one packet of Erichome Black T 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 the 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 colour of the sample changes to blue. Take the final reading of the counter.

<u>Calculation:</u>

Total hardness (mg/L as $CaCO_3$)
= Multiplying Factor (MF) x (Initial counter reading – Final counter reading)

$$\text{Where, } \mathbf{M.F.} = \frac{\text{Normality of EDTA x equivalent wt.of } CaCO_3 \text{ x } 1000}{\text{mL of sample taken}}$$

(Normality of EDTA titrant used in the lab is 0.002N)

Therefore for 100ml sample,
Total hardness (mg/L as $CaCO_3$) = final counter reading – initial counter reading

And for 50ml sample,
Total hardness (mg/L as $CaCO_3$) = 2× (final counter reading – initial counter reading)

Assignment Questions:

1. What is hardness and how it is caused? Discuss the environmental significance of hardness.
2. A water supply has 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 hardness of 315 mg/L as $CaCO_3$. Calculate carbonate hardness and non-carbonate hardness (in mg/L as $CaCO_3$) of the sample.

DATA SHEET

Experiment Name :
Experiment Date :

Student's Name :
Student's ID :
Year/ Semester :
Section :
Group :

Table

Sample No and source	Temperature of Sample (°C)	Volume of Sample (mL)	Burette Reading (mL)		Volume of EDTA solution (mL)	Hardness Concentration (mg/L as CaCO3)
			Initial	Final		

Signature of the course teacher and date