Somaiya Vidyavihar University, Mumbai.

Faculty of Engineering and Technology

Applied Chemistry Laboratory
Subject: Engineering Chemistry

CO-1: Understand the Importance of water in industry and methods to produce soft water and hard water.

Batch: C5-3 **Roll no: 54**

Name: Rajat Kumar

Date:

Experiment No: 8

Title: Water analysis - Determination of Chemical parameters

Aim: To determine the total hardness of water sample

Theory:

It is needless to emphasize the importance of water in our life. Without water, there is no life on our planet. We need water for different purposes. We need water for drinking, for industries, for irrigation, for swimming and fishing, etc.

Water for different purposes has its own requirements for composition and purity. Each body of water needs to be analyzed on a regular basis to confirm to suitability. The types of analysis could vary from simple field testing for a single analyte to laboratory based multi-component instrumental analysis. The measurement of water quality is a very exacting and time-consuming process, and a large number of quantitative analytical methods are used for this purpose.

Total hardness: Hardness in water is that characteristic, which "prevents the lathering of soap". This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap does not produce lather, but on other hand forms a white scum or precipitate. This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium.

Thus, water which does not produce lather with soap solution readily, but forms a white curd, is called hard water. On the other hand, water which lathers easily on shaking with soap solution, is called soft water. Such water consequently does not contain dissolved calcium and magnesium salts in it.

Temporary or carbonate hardness: It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, will produce insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of the vessel.

Permanent or non-carbonate hardness: It is due to the presence of chlorides and sulphates of calcium, magnesium, iron, and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as follows:

Soft	0-60mg/L
Medium	60-120mg/L
Hard	120-180mg/L
Very Hard	>180mg/L

In a hard water sample, the total hardness can be determined by titrating the Ca^{2+} and Mg^{2+} present in an aliquot of the sample with Na_2EDTA solution, using $NH_4Cl^-NH_4OH$ buffer solution of pH 10 and Eriochrome Black-T as the metal indicator.

Na_2H_2Y (*Disodium EDTA solution*) → $2Na^+$

H_2Y- Mg^{2+} + HD^{2-} (blue) → MgD (*wine red*) + H^+D (*metal-indicator complex, wine red color*) + H_2Y^-

→ Y^- (*metal EDTA complex colorless*) + HD^- (*blue color*) + H^+

Ethylenediamine tetra-acetic acid (EDTA) and its sodium salts form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome black T is added to an aqueous solution containing calcium and magnesium ions at a pH of 10 ± 0.1, the solution will become wine red. If EDTA is then added as a titrant, the calcium and magnesium will be complexed. After sufficient EDTA has been added to complex all the magnesium and calcium, the solution will turn from wine red to blue. This is the end point of the titration.

Units of Hardness:

1. Parts per million (ppm): Is the parts of calcium carbonate equivalent hardness per 10^6 parts of water, i.e., **1 ppm** = 1 part of $CaCO_3$ eq hardness in 10^6 parts of water.

2. Milligram per litre (mg/L): Is the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water. Thus:

1 mg/L = 1 mg of $CaCO_3$ eq hardness per L of water.

3. Clarke's degree (ºCl): Is number of grains (1/7000 lb) of $CaCO_3$ equivalent hardness per gallon (10 lb) of water. Or it is parts of $CaCO_3$equivalent hardness per 70,000 parts of water. Thus,

1ºCl = 1 grain of $CaCO_3$ eq hardness per gallon of water.

4. Degree French (ºFr): Is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water. Thus,

1º Fr = 1 part of $CaCO_3$ hardness eq per 10^5 parts of water.

Relationship Between Various Units of Hardness:

1ppm =1 mg/L=0.1ºFr =0.07ºCl

1mg/L=1 ppm=0.1°Fr = 0.07°Cl

1°Cl=1.43°Fr=14.3 ppm = 0.7°mg/L

1°Fr=10 ppm=10 mg/L = 0.7°Cl

$$\text{Total hardness as } CaCO_3 \text{ (ppm)} = \frac{\text{Vol. of EDTA(mL)} \times 0.1 \times \text{molarity of EDTA} \times 10^6}{\text{Vol. of the sample (mL)}}$$

Procedure:

- Under the chemical content, select the tests- Hardness, Alkalinity or COD.

A. **Determination of Hardness of Water Sample –**

1. Select the titrant.
2. Adjust the speed of the drops from the burette.
3. Adjust the molarity of titrant.
4. Select a definite volume of water sample.
5. Choose the indicator & start the titration.
6. When color changes from wine red to blue click the "stop" button & note the volume of EDTA used.
7. Then calculate the hardness of the water sample in ppm using the equation as follows.

$$\text{Total hardness as } CaCO_3 \text{ (ppm)} = \frac{\text{Vol. of EDTA(mL)} \times 0.1 \times \text{molarity of EDTA} \times 10^6}{\text{Vol. of the sample (mL)}}$$

Points to Remember while Performing the Experiment in a Real Laboratory:

1. Always wear a lab coat and gloves when you are in the lab. When you enter the lab, switch on the exhaust fan and make sure that all the chemicals and reagents required for the experiment are available. If it is not available, prepare the reagents using the components for reagent preparation.

2. Properly adjust the flame of the Bunsen burner. The proper flame is a small blue cone; it is not a large plume, nor is it orange.

3. Make sure to clean all your working apparatus with chromic acid and distilled water and ensure that all the apparatus are free from water droplets while performing the experiment.

4. Make sure to calibrate the electronic weight balance before taking the measurements.

5. Clean all glass wares with soap and distilled water. Once the experiment is completed recap the reagent bottles. Switch off the light, exhaust fan and Gas cylinder before leaving the lab.

6. Discard the used gloves in a waste bin.

Self-Evaluation:

1) The hardness of a water sample is usually a measure of

- ○ Na2+ and Mg2+
- ● Ca2+ and Mg2+
- ○ Na2+ and Cl-
- ○ Ca2+ and OH-

2) If the methyl orange alkalinity of the water equals or exceeds the total hardness, all the hardness is present as

- ○ Hydroxide hardness
- ○ Bicarbonate hardness
- ● Carbonate hardness
- ○ None of the above

3) COD is expressed in

- ● mg/L O2
- ○ mg/L
- ○ mg
- ○ L

4) In COD, the quantity of oxidant consumed is expressed in terms of its

- ● Oxygen equivalence
- ○ None of the above
- ○ Dissolved oxygen equivalence
- ○ Carbon equivalence

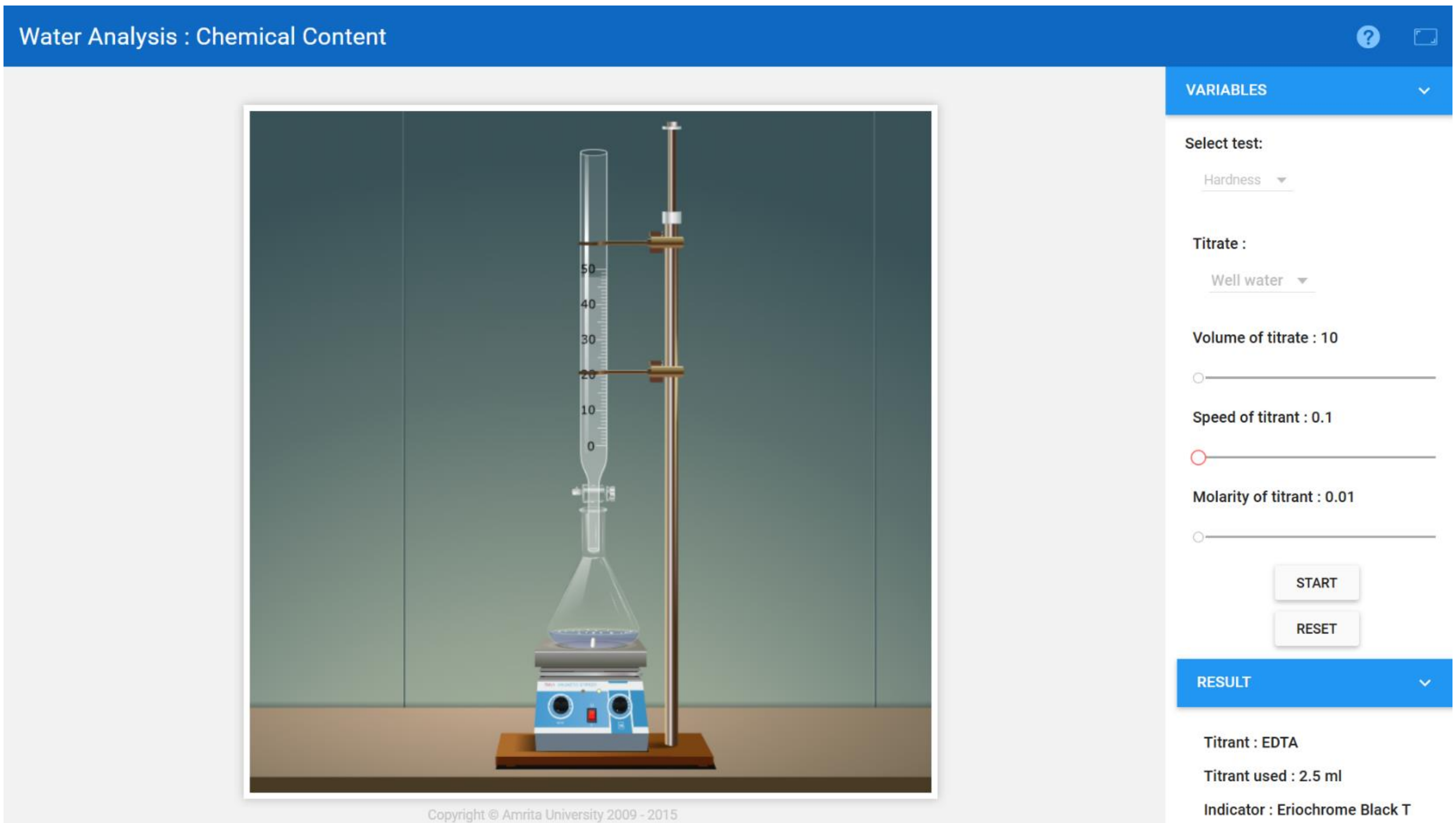
5) Alkalinity can be measured by titrating a sample with...........

- ● Strong acid
- ○ Strong base
- ○ Weak acid
- ○ Weak base

Observation:

PART 1: WELL WATER

Screenshot –



Burette : 0.01 M EDTA solution
Conical flask : 10 mL of sample + Indicator
Indicator : EBT (Eriochrome Black T)
End point : Wine Red to Blue

Reaction:

$(Ca^{+2} + Mg^{+2})$ + EBT + Buffer(pH 9-10) → (Ca-EBT + Mg-EBT) complex
(Hard water) (Indicator) (Unstable wine-red complex)

[Ca-EBT + Mg-EBT] complex + EDTA $\rightarrow$ EBT + [Ca-EDTA + Mg-EDTA] complex
(Unstable wine-red complex) (Blue) (Indicator) (Stable colorless complex)

Pilot Reading : ____ (mL) to _____ (mL)

Reading	I (mL)	II (mL)	Constant (mL)
Initial	0.00	0.00	
Final			
Difference			

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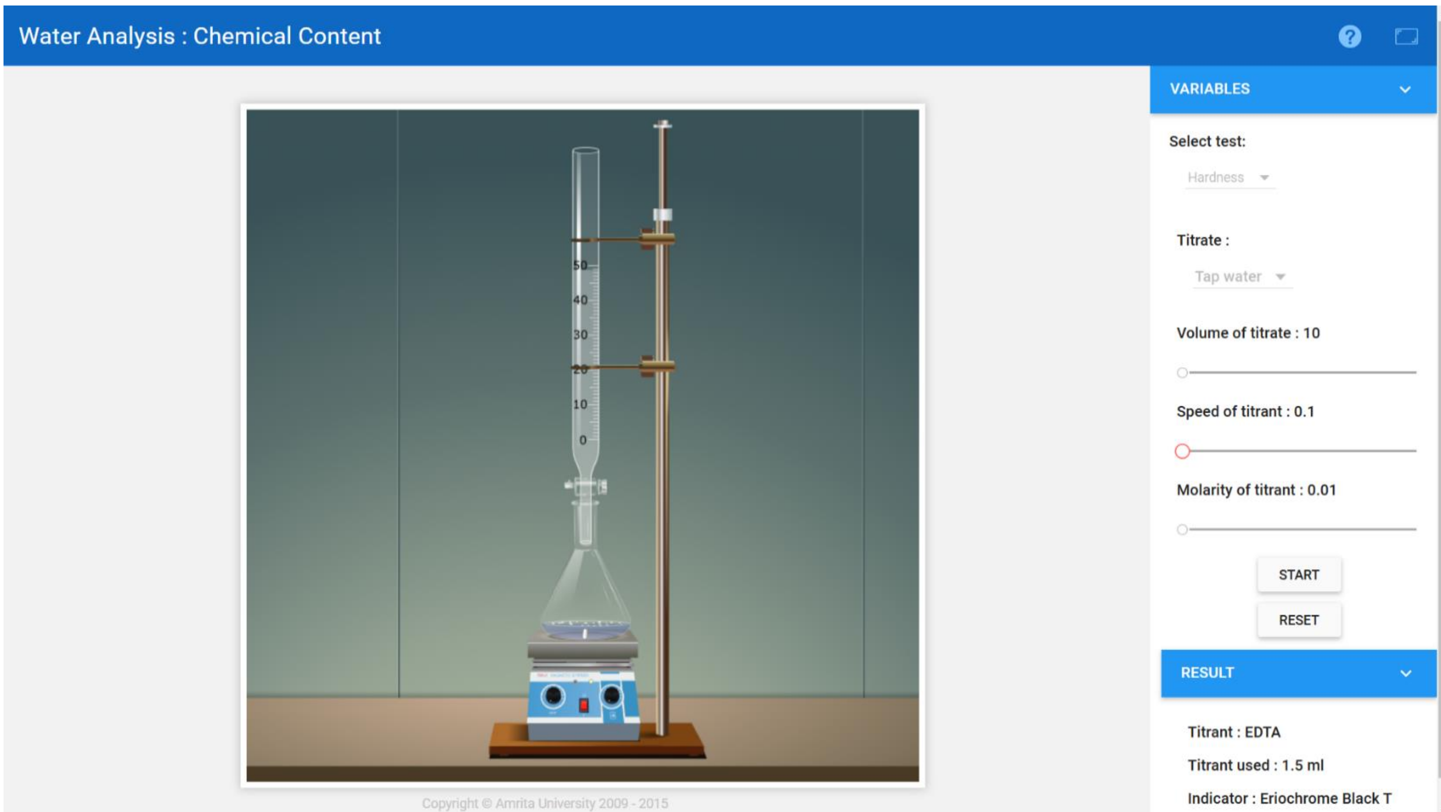
PART 2 - TAP WATER

Screenshot –



Burette : 0.01 M EDTA solution
Conical flask : 10 mL of sample + Indicator
Indicator : EBT
End point : Wine Red to Blue

Reaction:

$(Ca^{+2} + Mg^{+2})$ + EBT + Buffer(pH 9-10) → (Ca-EBT + Mg-EBT) complex
(Hard water) (Indicator) (Unstable wine-red complex)

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[Ca-EBT + Mg-EBT] complex + EDTA → EBT + [Ca-EDTA + Mg-EDTA] complex
(Unstable wine-red complex) (Blue) (Indicator) (Stable colorless complex)

Pilot Reading : ______ (mL) to ______ (mL)

Reading	I (mL)	II (mL)	Constant (mL)
Initial			
Final			
Difference			

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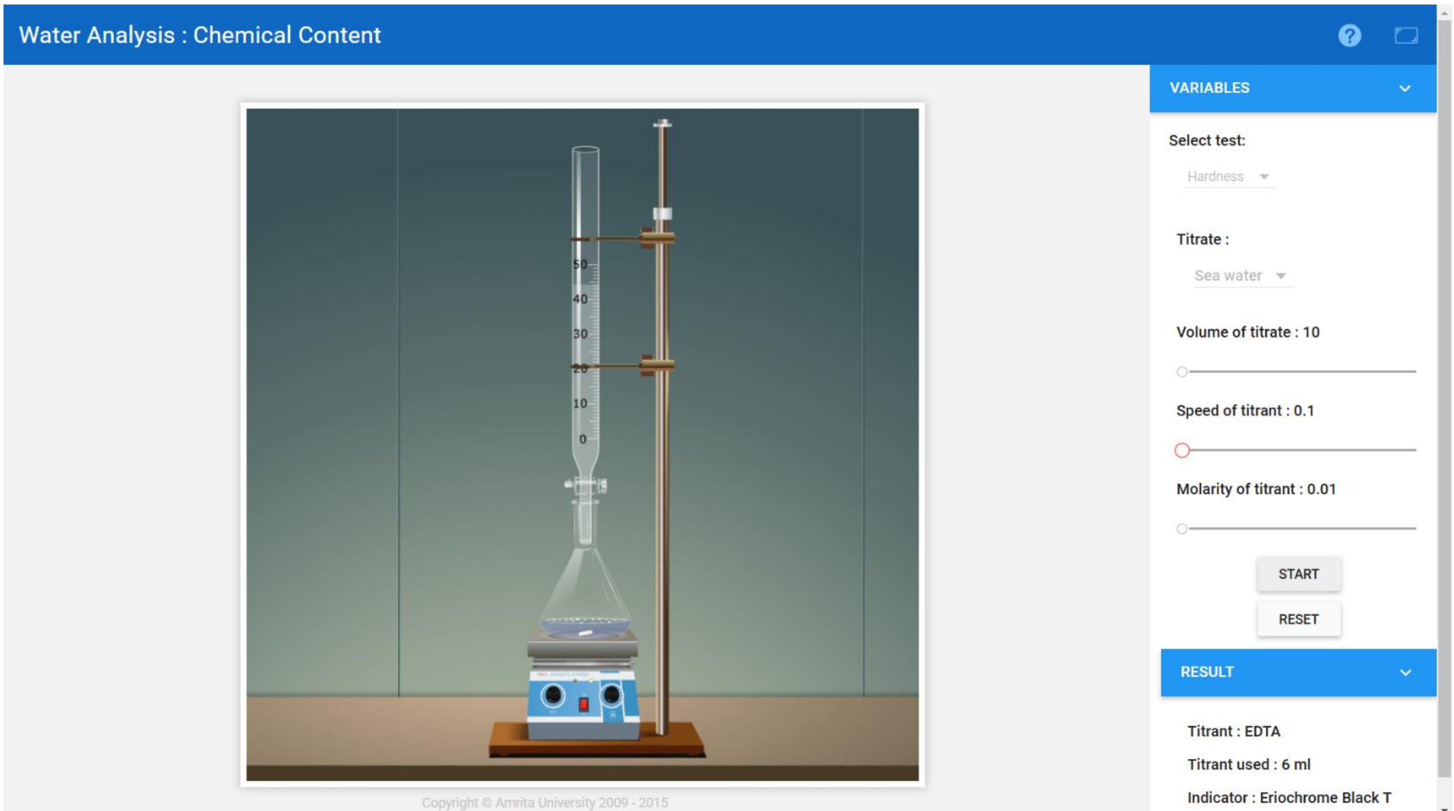
PART 3 - SEA WATER

Screenshot –



Burette	: 0.01 M EDTA solution
Conical flask	: 10 mL of sample + Indicator
Indicator	: EBT
End point	: Wine Red to Blue

Reaction:

$$\underset{\text{(Hard water)}}{(Ca^{+2} + Mg^{+2})} + \underset{\text{(Indicator)}}{EBT} + \text{Buffer(pH 9-10)} \rightarrow \underset{\text{(Unstable wine-red complex)}}{\text{(Ca-EBT + Mg-EBT) complex}}$$

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[Ca-EBT + Mg-EBT] complex + EDTA → EBT + [Ca-EDTA + Mg-EDTA] complex
(Unstable wine-red complex) (Blue) (Indicator) (Stable colorless complex)

Pilot Reading : _____ (mL) to _____ (mL)

Reading	I (mL)	II (mL)	Constant (mL)
Initial			
Final			
Difference			

Calculation:

Formula:

$$\text{Total Hardness (ppm)} = \frac{\text{Vol.of EDTA (ml)} \times 0.1 \times M_{EDTA} \times 10^6}{\text{Vol. of Sample (ml)}}$$

Part-1: Well water

Total Hardness (ppm) = $(2.5 \times 0.1 \times 0.01 \times 10^6) / 10 = 2500/10$
= **250 ppm**

Part-2: Tap water

Total Hardness (ppm) = $(1.5 \times 0.1 \times 0.01 \times 10^6) / 10 = 1500/10$
= **150 ppm**

Part-3: Sea water

Total Hardness (ppm) = $(6 \times 0.1 \times 0.01 \times 10^6) / 10 = 6000/10$
= **600 ppm**

Result: The hardness of **Sea Water** is the highest = **600 ppm**.

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Assignment:

1. **Convert the total hardness of water samples in ppm and meq/L from the following: A) 20.23 ^{o}Cl; B) 31.8 ^{o}Fr**

Ans: We know, 1 ppm = 0.07 ^{o}Cl = 0.1 ^{o}Fr = 0.02 meq/L

A) 20.23 ^{o}Cl

Since, 1 ppm = 0.07 ^{o}Cl

By unitary method, 20.23 ^{o}Cl = 20.23/0.07 = **289 ppm**

And now since, 1 ppm = 0.02 meq/L

By unitary method, 289 ppm = 289*0.02 = **5.78 meq/L**

B) 31.8 ^{o}Fr

Since, 1 ppm = 0.1 ^{o}Fr

By unitary method, 31.8 ^{o}Fr = 31.8/0.1 = **318 ppm**

And now since, 1 ppm = 0.02 meq/L

By unitary method, 318 ppm = 318*0.02 = **6.36 meq/L**

2. **A sample of water has hardness 208ppm $CaCO_3$ eqv. Find the hardness in terms of mg/L, ^{o}Fr, ^{o}Cl, meq/L.**

Ans: We know, 1 ppm = 1 mg/L = 0.1 ^{o}Fr = 0.07 ^{o}Cl = 0.02 meq/L

∴ 208 ppm = 208 mg/L = 20.8 ^{o}Fr = 14.56 ^{o}Cl = 4.16 meq/L

3. How many grams of FeSO4 dissolved per litre gives 210.5ppm of hardness?

Ans: We know, 1 ppm = 1 mg/L

Therefore, 210.5 ppm of hardness = 210.5 mg of Fe^{2+} ions per litre of solution

Now,

Moles of $Fe^{2+} = \frac{210.5\ mg}{Molar\ mass\ of\ Fe^{2+}} = \frac{210.5\ mg}{55.85\ g/mol} = \frac{0.2105\ g}{55.85\ g/mol}$

Moles of Fe^{2+} = **0.003769 mol**

Each mole of $FeSO_4$ provides one mole of Fe^{2+}, so the moles of $FeSO_4$ required are the same (i.e., 0.003769 mol)

Now, we have –

Moles of $FeSO_4$ = 0.003769 mol

Molar mass of $FeSO_4$ = 55.85+32+64 = 151.85 g/mol

Now, Mass of $FeSO_4$ = moles of $FeSO_4$ × molar mass of $FeSO_4$

= 0.003769 × 151.85

= **0.572 g**

Thus, to achieve a hardness of 210.5 ppm, you would need to dissolve approximately **0.572 grams** of $FeSO_4$ per liter of water.

4. Three samples were analyzed for their salt content:

(i) Sample A contains 168mg of magnesium carbonate per litre.

(ii) Sample B contains 820mg of calcium nitrate and 2mg of silica per litre.

(iii) Sample C contains 20g potassium nitrate and 2g calcium carbonate per 500ml. Determine the hardness in ppm and grains per gallon.

Ans: We know, 1 ppm = 0.58 gpg (since, 1 gpg = 17.1 ppm)
Therefore, hardness in gpg = hardness in ppm / 17.1

(i) Sample A: $MgCO_3$

Given: 168 mg/L of $MgCO_3$
Molar Mass of $MgCO_3$ = 84.31 g/mol
Molar Mass of Mg = 24.31 g/mol
Hardness in ppm: 168 mg/L × (24.31 / 84.31) = **48.44 ppm**
Hardness in gpg: 48.44 / 17.1 = **2.83 gpg**

(ii) Sample B: $Ca(NO_3)_2$ and SiO_2

Given: 820 mg/L of $Ca(NO_3)_2$ (Since, Silica does not contribute to hardness)
Molar Mass of $Ca(NO_3)_2$ = 164.1 g/mol
Molar Mass of Ca = 40.08 g/mol
Hardness in ppm = 820 mg/L × (40.08 / 164.1) = **200.28 ppm**
Hardness in gpg = 200.28 / 17.1 = **11.71 gpg**

(iii) Sample C: KNO_3 and $CaCO_3$

Given: 2 g of $CaCO_3$ in 500 mL (Since, KNO_3 does not contribute to hardness)
Concentration in 1 L: 2 × 2 = 4 g/L = 4000 mg/L
Molar Mass of $CaCO_3$ = 100.09 g/mol
Hardness in ppm = 4000 mg/L × (40.08 / 100.09) = **800.88 ppm**
Hardness in gpg = 800.88 / 17.1 = **46.84 gpg**

5. **Classify the following into temporary, permanent and non-hardness causing impurities: $Ca(HCO_3)_2$, $MgSO_4$, $CaCl_2$, CO_2, HCl, $Mg(HCO_3)_2$, $CaSO_4$, NaCl. How many grams of $CaCl_2$ dissolved per litre gives 150ppm of hardness?**

Ans: Classification of given impurities in Water Hardness:

Temporary Hardness: $Ca(HCO_3)_2$, $Mg(HCO_3)_2$

Permanent Hardness: $MgSO_4$, $CaCl_2$, $CaSO_4$

Non-Hardness Causing: CO_2, HCl, NaCl

Mass of $CaCl_2$ for 150 ppm Hardness:

$$\text{Mass of } CaCl_2 = \left(\frac{150\ mg/L\ CaCO3}{100.1\ g/mol}\right) \times 110.98\ \text{g/mol} = \mathbf{0.274\ g/L}$$

6. **Classify the following into carbonate and non-carbonate impurities and calculate all types of hardness-**
   $Mg(HCO_3)_2$ = 7.1mg/L, $Ca(HCO_3)_2$= 8.1mg/L, $MgCO_3$= 4.2mg/L, $CaCO_3$=10mg/L, $MgSO_4$= 24mg/L.

Ans:

Classification –

Carbonate impurities: $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, $MgCO_3$, $CaCO_3$

Non-carbonate impurities: $MgSO_4$

Hardness calculation –

For Carbonate Hardness:

$Mg(HCO_3)_2$: 7.1 mg/L × (100.1 / 146.34) = 4.85 mg/L as $CaCO_3$

$Ca(HCO_3)_2$: 8.1 mg/L × (100.1 / 162.11) = 5.00 mg/L as $CaCO_3$

$MgCO_3$: 4.2 mg/L × (100.1 / 84.31) = 4.98 mg/L as $CaCO_3$

$CaCO_3$: 10 mg/L (Given)

Total Carbonate Hardness = 4.85 + 5.00 + 4.98 + 10 = **24.83 mg/L** or **24.83 ppm**

For Non-Carbonate Hardness:

$MgSO_4$: 24 mg/L × (100.1 / 120.37) = 19.95 mg/L as $CaCO_3$

Total Non-Carbonate Hardness = **19.95 mg/L** or **19.95 ppm**

Thus, **Total Hardness = 24.83 + 19.95 = 44.78mg/L or 44.78ppm**

7. **0.28g $CaCO_3$ was dissolved in HCl and made upto 1L with distilled water. 100ml of this solution required 28ml EDTA solution. 100ml of hard water sample required 33ml of EDTA solution. After boiling, cooling and filtering, 100ml of the solution required 10ml of EDTA. Calculate hardness.**

Ans: Given: 1000 ml of SHW (Standard Hard Water) contains 0.28 gm of $CaCO_3$

i.e., 1000 ml of SHW contains 0.28 × 1000 = 280 mgs of $CaCO_3$

∴ 1 ml of SHW = 0.28 mg of $CaCO_3$

Now, 28 ml of EDTA = 100 ml of the SHW = 100 × 0.28 = 28 mgs of $CaCO_3$

1 ml of EDTA = 1 mgs of $CaCO_3$.

100 ml of hard water = 33 ml of EDTA = 33 × 1 = 33 mgs of $CaCO_3$

∴ 1000 ml of hard water = 33 × 1000/100 = 330 mgs of $CaCO_3$

Total hardness = 330 mg/L = 330 ppm

100 ml of the same water, after boiling, cooling and filtering required

= 10 ml of EDTA = 10 × 1 mgs of $CaCO_3$ = 10 mgs of $CaCO_3$

∴ 1000 ml of the water = 10 × 1000/100 = 100 mgs of $CaCO_3$

Permanent hardness = 100 mg/L = 100 ppm

Temporary hardness = Total hardness − permanent hardness

Temporary hardness = 330 – 100 **= 230 mg/L = 230 ppm**