

# STUDY MODULE- III

## Water Chemistry

(Physico-chemical Analysis of Water)

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## General course information

### Course Details

#### MODULE III FOR ANALYSIS OF PHYSICO CHEMICAL PARAMETERS OF WATER

**Coordinating Unit:** Pakistan Council of Research in Water Resources

**Duration:** 6 months

**Location:** Islamabad

**Units:** 7

### Course Description

#### Course Learning Outcomes:

On successful completion of this course students will be able to:

- 1 Explain basic water chemistry
- 2 Identify the parameters that are involved in characterizing the drinking water safe or unsafe
- 3 Recognize the difference between physical and chemical parameters
- 4 Explain the importance of water quality tests and the use of different instruments for water quality tests in laboratory and on site testing.
- 5 Perform water quality testing in laboratory and on-site Learning resources

**Learning and teaching activities:** Students will be engaged in the diploma course by giving lectures, laboratory demonstration and field visits.

#### Assessment:

- Assessment must encourage and reinforce learning.
- Assessment must enable robust and fair judgments about student performance.
- Assessment practices must be fair and equitable to students and give them the opportunity to demonstrate what they have learned.
- Assessment must maintain academic standards.

**Assessment Summary:** Assessment will be purely done on the best analytical capabilities of student like working on the instrument, calibration, preparation of standards, reporting of result etc

**Student feed back:** Feedback will be sought from students in a variety of ways including on-going engagement with staff, the use of group discussion and the use of Student Experience of Learning and Teaching.

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## Abbreviation

Sr. No.	Abbreviation	Expanded Form
1.	L	Liter
2.	mL	Milliliter
3.	ppm	Parts per million
4.	gm	Gram
5.	mg	Milligram
6.	mg/L	Milligram per litre
7.	M	Molar solution
8.	N	Normal solution

## Chemical formulas

Sr. No.	Chemical formulas	Names of Reagents
1.	EDTA	Ethylenediaminetetraaceticacid disodium salt dihydrate
2.	NaOH	Sodium hydroxide
3.	CaCO <sub>3</sub>	Calcium carbonate
4.	NH <sub>4</sub> OH	Ammonium hydroxide
5.	Conc.HCl	Concentrated Hydrochloric acid
6.	AgNO <sub>3</sub>	Silver nitrate
7.	NaCl	Sodium chloride
8.	EBT	Eriochrome black T
9.	AgCl	Silver Chloride



# Unit 1: Calcium

## 1 Calcium

### 1.1 Introduction:

Calcium is a mineral that is necessary for life and the fifth-most abundant element in the human body. In addition to building bones and keeping them healthy, calcium enables our blood to clot, our muscles to contract, and our heart to beat. About 99% of the calcium in our bodies is in our bones and teeth. Calcium is a chemical element with the symbol Ca and atomic number 20.

### 1.2 Occurrence:

The most common calcium compound on earth is calcium carbonate, found in limestone. Water calcium result from passage through or over deposits of lime stone, dolomite, gypsum and other minerals. Calcium contributes to total hardness of water.

### 1.3 Food sources:

Foods rich in calcium include dairy products, such as yogurt and cheese, sardines, salmon, soy products, kale, and fortified breakfast cereals.

### 1.4 Health Impacts:

Calcium deficiency has been associated with increased risks of osteoporosis and osteomalacia. Calcium generally does not pose any health problems.

### 1.5 Other effects:

At high levels (in combination with magnesium), it can cause incrustations on utensils and scale deposits in water heaters and boiler tubing. It also reduces soap lather.

### 1.6 Treatment methods:

Methods used to reduce calcium and associated hardness include

- Chemical softening treatment
- Reverse osmosis
- Electro dialysis: Electro dialysis (Figure:1) is an advanced membrane technology process that utilizes ion movement to desalinate water.
- Ion exchange

# Electro dialysis

Electrodialysis reversal utilizes a membrane, like that in reverse osmosis, but sends an electric charge through the solution to draw metal ions to the positive plate on one side, and other ions (like salt) to the negative plate on the other.

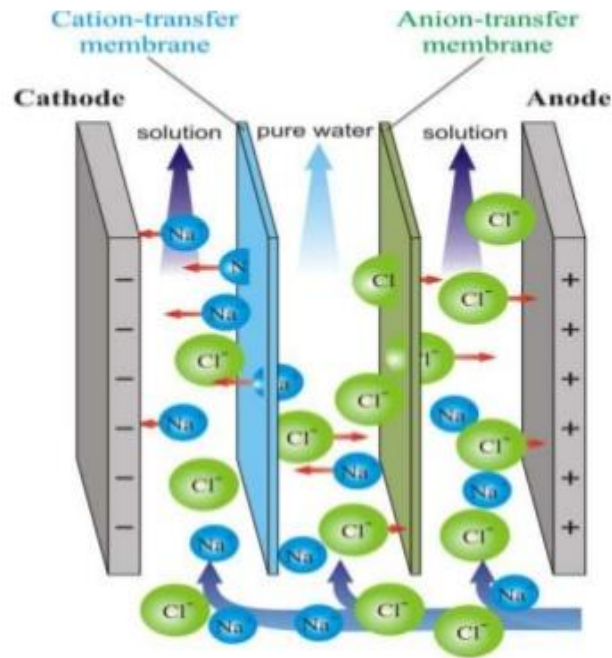


Figure 1: Electrodialysis

## 1.7 Determination of Calcium:

## 1.8 Testing methods:

Generally calcium is analyzed by titration method. Other high tech methods involve equipment like auto-titrators and ion chromatographs, atomic absorption spectrophotometric method and inductively coupled plasma method.

## 1.9 Standard Operating Procedure for Calcium by EDTA Titrimetric Method:



*Figure 2: Titration Method*

## 1.10 Principle of Measurement:

When EDTA is added to water containing both calcium and magnesium, EDTA combines first with calcium. When sodium hydroxide buffer is added to water magnesium is precipitated as magnesium hydroxide and EDTA combines with calcium only. A color change is observed when all the calcium is titrated with EDTA at a pH of 12-13.

## 1.11 Reagents and Standards:

- EDTA (0.01M)
- NaOH (1M)
- Murexide Indicator
- Distilled Water
- $\text{CaCO}_3$
- HCl
- methyl red indicator
- N  $\text{NH}_4\text{OH}$

## 1.12 Preparation of reagents

### 1.12.1 0.01M EDTA :

- Weigh 3.7224g of EDTA analytical grade (GR grade).
- Dissolve it in distilled water by shifting to 1000 mL Volumetric Flask.
- Make the volume up to the mark with distilled water

### 1.12.2 NaOH (1M):

- Weigh out 4g of sodium hydroxide.
- Quantitatively transfer to 100 mL Volumetric Flask.
- Make the volume up to the mark with distilled water.

### 1.12.3 Murexide Indicator:

- Weigh 100 g murexide dye and 100g sodium chloride salt in dry form.
- Grind and mesh it to fine powder form.

### 1.12.4 Methyl red indicator:

Dissolve 100 mg methyl red sodium salt in distilled water and dilute 200 mL

## 1.13 Standardization Procedure:

- Weigh 1.0 gm anhydrous calcium carbonate powder into a 500 mL flask.
- Place a funnel in the flask neck and add, a little at a time, 1+1 HCl until all  $\text{CaCO}_3$  has dissolved.
- Add 200 mL distilled water and boil for a few minutes to expel  $\text{CO}_2$ .
- Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3 N  $\text{NH}_4\text{OH}$  or 1+1 HCl, as required.
- Transfer quantitatively and dilute to 1000 ml with distilled water.
- 1 mL=1mg  $\text{CaCO}_3$ .

## 1.14 Calculation

$$\text{Ca mg/L} = \frac{A \times B \times 400}{\text{mL sample}}$$

Where

A= mL titration for sample and

B= mg  $\text{CaCO}_3$  equivalent to 1.00 ML EDTA titrant.

## 1.15 Procedure for analysis of sample



- Take 10 mL sample in 100 mL beaker and add 10 mL of deionized water in it.
- Maintain the pH (12) of the sample with 1M NaOH and add pinch of Murexide (ammonium purpurate) indicator.
- Shake it till the indicator get dissolved and pink color is produced.
- Then titrate it against the EDTA (0.01 M). EDTA solution should be added slowly with constant stirring till color changes from pink to purple color (end point).
- Multiply the EDTA burette reading with 40, this will be equal to the calcium concentration in the sample.
- Number of replicates to be analyzed is “Three” for each sample.

### 1.16 Quality Control:

- EDTA concentration is verified by titrating with known standards of Ca.
- Method blank is analyzed after every 10 samples
- Laboratory Control samples of 10 & 100 ppm Calcium analyzed with every batch of 10 samples.

### 1.17 Expression of Results:

The Calcium is measured in mg/L.

### 1.18 Safety precautions:

- Never smell and taste chemicals. Never pipette with mouth.
- Use chemical fume hood for preparation of reagents
- Report damaged equipment or glassware to your supervisor
- Do not eat or drink in the laboratory.

### 1.19 Checklist for testing of calcium:

Sr no.	Checklist for testing	Yes/No
1.	Lab demonstration of calcium testing	
2.	Glass ware washing	
3.	Preparation of Reagents and standards	
4.	Standardization of solutions	
5.	Perform testing	
6.	Result calculation	

### **1.20 Planned Demonstration:**

Testing of calcium in Chemical Lab-II (Reagents preparation, glassware washing, standards preparation, testing, quality control, calculations and reporting, units conversion).

### **1.21 Class Exercises:**

- Surprise tests
- Analysis of unknown samples
- Quiz/Tutorials
- Lab demonstration test

### **1.22 Group project:**

Water Quality Assessment

## UNIT 2: Total Hardness

### 2 Total Hardness

#### 2.1 Introduction:

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in mg/L.

OR

It is the capacity of water to precipitate soap. Soap is chiefly precipitated by the calcium and magnesium ions present.

#### 2.2 Sources of hardness in water:

The principal natural **sources** of **hardness** in **water** are dissolved metallic ions from sedimentary rocks, seepage and runoff from soils. Calcium and magnesium, the two principal ions, are present in many sedimentary rocks, the most common being limestone and chalk.

Water hardness is usually expressed in terms of parts per million (ppm) or milligrams per liter (mg/L).

#### 2.3 Effects of hardness:

- Hardness prevents soap from lathering by causing the development of an insoluble curdy precipitate in the water; referring to the soap wasting properties of hard water.
- Hardness typically causes the buildup of hardness scale on dishes and glassware
- Dissolved calcium and magnesium salts are primarily responsible for most scaling in pipes and water heaters and cause numerous problems in laundry, kitchen, and bath.
- Hairs become sticky after washing with hard water
- High soap usage & need for fabric softeners
- High energy costs, possibly due to scale build-up in pipes and on appliances
- Scale build up in sinks, tubs, faucets & appliances

#### 2.4 Techniques to remove hardness:

- Chemical softening—lime softening, hot and cold; lime-soda softening
- Membrane separation softening—Nano filtration
- Cation exchange softening—inorganic, carbonaceous, or organic base exchangers

## 2.5 Determination of hardness:

## 2.6 Testing methods:

Generally hardness is analyzed by titration method. Other high tech methods involve equipment like auto-titrators (Figure 2) and ion chromatograph and calculation method.



*Figure 3: Auto-titrator*

## 2.7 Standard Operating Procedure for Total Hardness by EDTA Titrimetric Method:



*Figure 4: Titration method*

### **2.7.1 Principle of Measurement:**

When EDTA is added to water containing both calcium and magnesium, it combines first with calcium and then magnesium, when pH is made sufficiently high. If a small amount of EBT (Eriochrome Black T) indicator is added to an aqueous solution containing calcium and magnesium ions, solution becomes wine red.

#### **2.7.1.1 Reagents:**

- EDTA (0.01M)
- Buffer Inhibitor
- Erichrome black T
- Distilled Water
- Hardness Stock Solution (1000ppm)

#### **2.7.1.2 Preparation of Reagents:**

(a) 0.01M EDTA:

- Weigh 3.7224g of EDTA analytical grade (GR grade).
- Dissolve it in distilled water by shifting to 1000 mL Volumetric Flask.
- Make the volume up to the mark with distilled water.

#### **2.7.2 (b) Buffer Inhibitor Mixture:**

#### **2.7.3 Reagents:**

- Conc. HCl
- 2-Aminoethanol
- Magnesium salt of EDTA

#### **2.7.4 Procedure:**

Mix 55 mL Conc. HCl with 400ml deionized water and then, slowly and stirring add 300mL of 2-aminoethanol. Add 5g Magnesium salt of EDTA and dilute to 1 litre with de-ionized water.

#### **2.7.4.1 Standardization of EDTA:**

#### **2.7.4.2 Reagents:**

- $\text{CaCO}_3$
- HCl
- methyl red indicator
- 3 N  $\text{NH}_4\text{OH}$

#### **2.7.4.3 Standardization Procedure:**

Weigh 1.0 gm anhydrous calcium carbonate powder into a 500 ml flask .Place a funnel in the flask neck and add, a little at a time, 1+1 HCl until all  $\text{CaCO}_3$  has dissolved. Add 200 ml distilled water and boil for a few minutes to expel  $\text{CO}_2$ . Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3 N  $\text{NH}_4\text{OH}$  or 1+1 HCL, as required.

Transfer quantitatively and dilute to 1000 ml with distilled water.;

$$1 \text{ mL} = 1 \text{ mg } \text{CaCO}_3.$$

#### **2.7.4.4 Calculation:**

$$\text{Total hardness ( EDTA) as mg } \text{CaCO}_3/\text{L} = \frac{A \times B \times 1000}{\text{mL sample}}$$

Where

A= mL titration for sample and

B= mg  $\text{CaCO}_3$  equivalent to 1.00 ml EDTA titrant.

#### **2.7.4.5 Procedure for analysis of sample:**

1. Take 10 mL sample in 100 mL beaker and add 20 mL of deionized water in it
2. Add 1 mL of Buffer inhibitor in sample.
3. Add small amount of EBT indicator in it and shake it till the indicator get dissolved and wine red color is produced.
4. Titrate the above solution against the EDTA (0.01 M) from the (burette with 0.05 mL and 0.02 mL resolution are used) EDTA solution should be added slowly with constant stirring till the sky blue color appeared (end point).
5. Multiply the EDTA burette reading with 100, this will be equal to the total hardness of the sample.
6. Number of replicates to be analyzed is “Three” for each sample.

### **2.8 Quality Control**

- EDTA concentration is verified by titrating with known standards of Ca.
- Method blank is analyzed after every 10 samples
- Laboratory Control samples of 100 & 250 ppm analyzed with every batch of 10 samples.

### **2.9 Expression of Results:**

The hardness is measured in mg/L.

## 2.10 Safety precautions:

- Never smell and taste chemicals. Never pipette with mouth.
- Use chemical fume hood for preparation of reagents
- Report damaged equipment or glassware to your supervisor
- Do not eat or drink in the laboratory.

## 2.11 Checklist for testing of hardness

Sr no.	Checklist for testing	Yes/No
1.	Lab demonstration of hardness testing	
2.	Glass ware washing	
3.	Preparation of Reagents and standards	
4.	Standardization of solutions	
5.	Perform testing	
6.	Result calculation	

## 2.12 Planned Demonstration:

Testing of hardness in Chemical Lab-II (Reagents preparation, glassware washing, standards preparation, testing, quality control, calculations and reporting, units conversion)

## 2.13 Class Exercises:

- Surprise tests
- Analysis of unknown samples
- Quiz/Tutorials
- Lab demonstration test

## 2.14 Group project:

Water Quality Assessment

## Unit 3: Magnesium

### 3 Magnesium

#### 3.1 Introduction:

Magnesium is present in seawater in amounts of about 1300 ppm. After sodium, it is the most commonly found cation in oceans. Rivers contains approximately 4 ppm of magnesium, marine algae 6000-20,000 ppm, and oysters 1200 ppm. The human body contains about 25 g of magnesium, of which 60% is present in the bones and 40% is present in muscles and other tissue. It is a dietary mineral for humans. Magnesium is an ingredient of many enzymes.

Symbol of magnesium is Mg and atomic number 24 with +2 valency. Measuring unit of magnesium is ppm (mg/L)

#### 3.2 Sources:

A large number of minerals contains magnesium, for example dolomite (calcium magnesium carbonate;  $\text{CaMg}(\text{CO}_3)_2$ ) and magnesite (magnesium carbonate;  $\text{MgCO}_3$ ). Magnesium is washed from rocks and subsequently ends up in water. Magnesium is usually less abundant in water than calcium since magnesium is found in earth's crust in much lower amounts as compared with calcium.

Magnesium has many different purposes and consequently may end up in water in many different ways. Chemical industries add magnesium to plastics and other materials as a fire protection measure or as a filler. It also ends up in the environment from fertilizer application and from cattle feed. Magnesium sulphate is applied in beer breweries, and magnesium hydroxide is applied as a flocculant in wastewater treatment plants. Magnesium is also a mild laxative. Magnesium alloys are applied in car and plane bodies. During World War II magnesium was applied in fire bombs, to cause major fires in cities.

#### 3.3 Health impacts:

Magnesium is essential for human body. It is an element that is essential to plant and animal nutrition. An adult body contains around 25 gram (g) of magnesium, 50–60% of which the skeletal system stores. The rest is present in muscle, soft tissues, and bodily fluids. Magnesium is needed for more than 300 biochemical reactions in the body. It helps to maintain normal nerve and muscle function, supports a healthy immune system, keeps the heartbeat steady, and helps bones remain strong. It also helps adjust blood glucose levels. It aids in the production of energy and protein.



### **3.4 Other Effects:**

Elevated levels of magnesium (in combination with calcium) can cause incrustations on utensils and water heaters and consume soap lather.

### **3.5 Dietary source:**

Doctors link magnesium deficiency with a range of health complications, so people should aim to meet their daily recommended levels of magnesium. Many foods contain high levels of magnesium, including nuts and seeds, dark green vegetables, whole grains, and legumes. Manufacturers also add magnesium to some breakfast cereals and other fortified food

An overdose of magnesium through dietary sources is unlikely because the body will eliminate any excess magnesium from food through urine. However, a high intake of magnesium from supplements can lead to gastrointestinal problems, such as diarrhea, nausea, or cramping.

### **3.6 Treatment process:**

### **3.7 Water Softening (Ion Exchange):**

Magnesium compounds are usually removed from water, because of the role magnesium plays in water hardness. Water softeners are typically used to remove calcium and magnesium hardness in water by an exchange process. The calcium and magnesium are removed from the water and sodium is added in their place.

### **3.8 Determination of magnesium**

Evaluating Magnesium by Calculation method:

Once calcium and total hardness is analyzed by EDTA titrimetric method, their results are used in calculation of magnesium in same sample by using formula written below

Calculate Magnesium by using the formula

- $\text{mg Mg/L} = (\text{Total Hardness (as mg CaCO}_3\text{/l)} - \text{calcium hardness (as mg CaCO}_3\text{/L)}) \times 0.243$
- Where calcium hardness is calculated by multiplying Ca with 2.5

## Unit 4: Alkalinity

### 4 Alkalinity

#### 4.1 Introduction:

Alkalinity is defined as the sum of all the titratable bases present in water.

or

It is the acid neutralizing capacity of water. More accurately, the alkalinity of a water mainly comprises the sum of the bicarbonates, carbonates and hydroxides of calcium, magnesium, sodium and potassium. It is taken as an indication of the concentration of these constituents.

‘Alkalinity’ is taken to mean the opposite of ‘acidity’ i.e. as the pH value increases alkalinity increases. Calcium and magnesium bicarbonates predominate in waters and comprise the temporary hardness of a water. Where the alkalinity is less than the total hardness, the excess hardness is termed permanent hardness. Conversely, where the alkalinity is greater than the total hardness, the excess alkalinity is usually due to the presence of sodium bicarbonate, which does not affect the hardness of the water. Because bicarbonate ions can exist at pH values below pH 7.0, a measurable alkalinity is still obtained with ‘acidic’ waters down to pH values of 4.5.

#### 4.2 Sources of Alkalinity:

Alkalinity in freshwater systems is derived from several sources like weathering of rocks and soil, exchange reactions in soils, biological uptake and reduction of strong acid anions, evaporation and precipitation of minerals, and atmospheric deposition of dust. The evaporation process also has indirect effects on the alkalinity of some systems, such as salt lakes. In lakes where evaporation greatly exceeds freshwater inputs, the solubility product of many minerals may be exceeded and precipitates will form. Typically the first minerals to precipitate are calcium and magnesium carbonates.

In natural water, most  $H^+$  of the alkalinity is due to  $CO_2$ . The free  $CO_2$  dissolves in water to form carbonic acid ( $H_2CO_3$ ), which further dissociates into  $H^+$  and  $HCO_3^-$ . Thus,  $HCO_3^-$  formed further dissociates into  $H^+$  and  $CO_3^{2-}$ .

#### 4.3 Why we measure alkalinity?

- Determining the suitability of water for irrigation
- Interpretation and control of water and waste water treatment processes

- Alkalinity provides a buffering effect on pH, which is an important factor in many water treatment processes. It is also a key factor in determining the corrosive or aggressive nature of a water
- Alkalinity also protects our water from acid rain. Below is a picture of how alkalinity protects the water's pH and its wildlife.

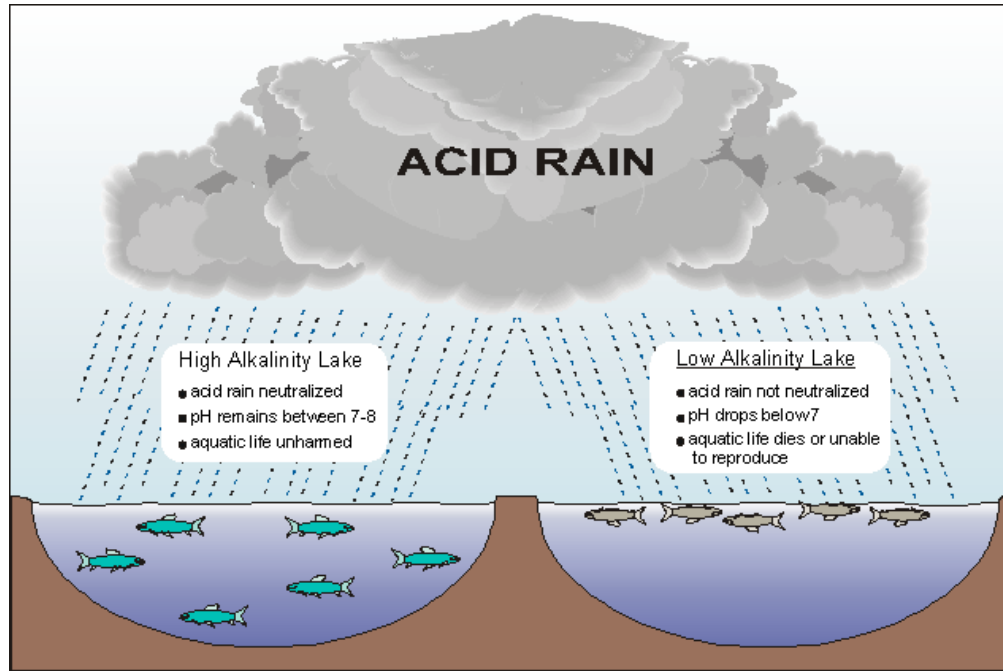


Figure 5: Alkalinity protects the water's pH and its wildlife

#### 4.4 Treatment:

Ion exchange resins and boilers are used to remove alkalinity.

#### 4.5 Chloride Ion exchange resin:

It contains strong base anion exchange resin that exchanges chloride (the  $\text{Cl}^-$  ion of the  $\text{NaCl}$ ) for carbonate ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ). As water passes through the anion resin the carbonate, bicarbonate and sulfate ions are exchanged for chloride ions.

#### 4.6 Boiling Method:

Carbonate and bicarbonate alkalinities are decomposed by heat in boiler water releasing carbon dioxide into the steam. This gas combines with the condensed steam in process equipment and return lines to form carbonic acid. This depresses the pH value of the condensate returns and results in corrosive attack on the equipment and piping.

## 4.7 Determination of alkalinity:



*Figure 6: Titration method*

## 4.8 Principle of Measurement:

Alkalinity is determined by titration of the sample with a standard solution of a strong mineral acid.

## 4.9 Reagents:

- Hydrochloric Acid solution (0.1N)
- Hydrochloric Acid solution (0.02N)
- Sodium carbonate solution (0.05N)
- Sodium carbonate solution(0.05N)
- Mixed indicator

## 4.10 Preparation of mixed indicator:

Weigh and dissolve bromocresol green sodium salt (0.1g) and methyl red sodium salt(0.02g) in 100 mL distilled water

## 4.11 Preparation and Standardization Of 0.1N Hydrochloric Acid:

### 4.11.1 Reagents :

- Conc. Hydrochloric acid (37%AR)
- 0.05 N Standardized  $\text{Na}_2\text{CO}_3$
- Distilled water
- Bromocresol and methyl red indicator

### 4.11.2 Preparation of 0.05N $\text{Na}_2\text{CO}_3$ :

- Weigh 2.6767g of  $\text{Na}_2\text{CO}_3$  and transfer in 1000 mL flask.

- Dilute to mark with distilled water.

#### **4.11.3 Preparation of 0.1N Hydrochloric Acid:**

- Take 8.3 mL of Conc. HCl (usually 32%) in 1000 mL flask
- Dilute to mark with distilled water. At this point concentration of acid solution should be 0.1 M

#### **4.11.4 Standardization of 0.1N Hydrochloric Acid :**

- Pipette 10 mL of the prepared HCl standard and transfer to a beaker.
- Titrate it against 0.05 N  $\text{Na}_2\text{CO}_3$  by using mixed indicator.
- Repeat to confirm result.
- From the titration calculate the concentration of the prepared HCl solution
- Using the calculation, calculate the amount of distilled water which must be added to the original solution to give a desired concentration solution Once the calculated volume has been added, mix thoroughly and re-titrate with the standardized  $\text{Na}_2\text{CO}_3$  to ensure the desired concentration has been achieved.

### **4.12 Preparation and Standardization of 0.02N Hydrochloric Acid:**

#### **4.12.1 Reagents:**

- 0.1N HCl
- 0.05N  $\text{Na}_2\text{CO}_3$
- Distilled water
- mixed indicator

#### **4.12.2 Preparation:**

- Take 200 mL of 0.02N HCl in 1000 mL flask
- Dilute to mark with distilled water

#### **4.12.3 Standardization:**

- Pipette 10 mL of the prepared 0.02N HCl standard and transfer to a beaker.
- Titrate it against 0.05 N  $\text{Na}_2\text{CO}_3$  by using mixed indicator. Repeat to confirm result.
- From the titration check and calculate the concentration of the prepared HCl solution

### **4.13 Procedure for analysis of sample:**

- To 10 mL of sample few drops of mixed indicator is added.
- It is titrated against 0.02 N HCl

- 25 mL burette with 0.05 mL resolution is used for titration, for low alkalinity less than 50mg/L, 10ml burette with 0.02 mL resolution is used.
- Titration is stopped when sample color changed to pink.
- The total Alkalinity is calculated by using following formula

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times N \times 50000}{\text{ml sample}}$$

Where:

A = ml standard acid used

N = Normality of the standard acid

- Number of replicates to be analyzed are “Three” for each sample.

#### 4.14 Quality Control:

- Method blank is analyzed after every 10 samples
- Laboratory Control samples of 50ppm and 100ppm analyzed with every batch of 10 samples.
- NWQL check repeatability by reanalyzing a pre-analyzed sample once a day

#### 4.15 Expression of results:

The alkalinity is measured in mg/L.

#### 4.16 Safety precautions:

- Never smell and taste chemicals. Never pipette with mouth.
- Use chemical fume hood for preparation of reagents
- Report damaged equipment or glassware to your supervisor
- Do not eat or drink in the laboratory.

#### 4.17 Checklist for testing of alkalinity

Sr no.	Checklist for testing	Yes/No
1.	Lab demonstration of alkalinity testing	
2.	Glass ware washing	
2.	Preparation of Reagents and standards	
3.	Standardization of solutions	

4.	Perform testing	
5.	Result calculation	

#### **4.18 Planned Demonstration:**

Testing of alkalinity in Chemical Lab-II (Reagents preparation, glassware washing, standards preparation, testing, quality control, calculations and reporting, units conversion)

#### **4.19 Class Exercises:**

- Surprise tests
- Analysis of unknown samples
- Quiz/Tutorials
- Lab demonstration test

#### **4.20 Group project:**

Water Quality Assessment

## Unit 5: Bicarbonates

### 5 Bicarbonates

#### 5.1 Introduction:

Alkalinity of many surface water is primarily a function of carbonate, bicarbonate and hydroxide content. In natural waters, the alkalinity is usually caused by bicarbonate. Bicarbonate alkalinity is present if carbonate alkalinity is less than half of the total alkalinity and is calculated by following formula.

$$\text{HCO}_3 = \text{T} - 2\text{P}$$

Where

T is total alkalinity

P is phenolphthalein/alkalinity

If carbonates are absent then

$$\text{HCO}_3 = \text{Total alkalinity}$$

#### 5.2 Health impacts:

Bicarbonate is a major element in our body. Secreted by stomach it is necessary for digestion. It reduces the acidity of dietary components. It has a prevention effect on dental cavities. Lactic acid produced during exercise (causing acidification of PH in blood) is buffered by bicarbonate. Bicarbonate rich mineral water could be useful in prevention of calcium oxalate and uric acid renal stones

Bicarbonate ( $\text{HCO}_3^-$ ) is a vital component of the pH buffering system of the human body (maintaining acid–base homeostasis). 70%–75% of  $\text{CO}_2$  in the body is converted into carbonic acid ( $\text{H}_2\text{CO}_3$ ), which is the conjugate acid of  $\text{HCO}_3^-$  and can quickly turn into it. Bicarbonate also serves much in the digestive system. It raises the internal pH of the stomach, after highly acidic digestive juices have finished in their digestion of food. Bicarbonate also acts to regulate pH in the small intestine. It is released from the pancreas in response to the hormone secretin to neutralize the acidic chyme entering the duodenum from the stomach.

#### 5.3 Other Uses

The most common salt of the bicarbonate ion is sodium bicarbonate,  $\text{NaHCO}_3$ , which is commonly known as baking soda. The flow of bicarbonate ions from rocks weathered by the carbonic acid in rainwater is an important part of the carbon cycle.



# Unit 6: Carbonates

## 6 Carbonates

### 6.1 Introduction:

Carbonates in water comes from the percolation of water through deposits of limestone, chalk or gypsum which are largely made up of calcium and magnesium carbonates, bicarbonates and sulphates . When dissolved, these type of minerals yield calcium and magnesium cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and carbonate and bicarbonate anions ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ).

Carbonate materials and limestone are two elements that can buffer pH changes in water. Calcium carbonate ( $\text{CaCO}_3$ ) and other bicarbonates can combine with both hydrogen and hydroxyl ions to neutralize pH. When carbonate minerals are present in the soil, the buffering capacity (alkalinity) of water is increased, keeping the pH of water close to neutral even when acids or bases are added. Additional carbonate materials beyond this can make neutral water slightly basic.

Seawater has a pH around 8.2, though this can range between 7.5 to 8.5 depending on its local salinity. pH levels will increase with salinity until the water reaches calcium carbonate ( $\text{CaCO}_3$ ) saturation. The oceans generally have a higher alkalinity due to carbonate content and thus have a greater ability to buffer free hydrogen ions.

As we increase the pH, we see that between 4.3 and 8.3, the dissolved carbon dioxide starts to convert to bicarbonate ion. This conversion is complete at a pH of about 8.3, where only bicarbonate is present. Increasing the pH beyond 8.3, the bicarbonate ion is converted to carbonate ion. Conversion is nearly complete at a pH around 10.2 with almost all the bicarbonate being converted to carbonate. Further increasing the pH past 10.2, we start seeing measurable levels of hydroxide ions along with the carbonate ions.

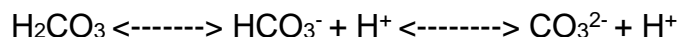
Inter Conversion of carbonates and bicarbonates:

Carbonic acid is formed when carbon dioxide gas is dissolved in water.

$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$ . These are the salts of carbonic acid.

- Formula of Carbonate ion:  $\text{CO}_3^{2-}$
- Formula of Bicarbonate ion:  $\text{HCO}_3^-$

These anions are formed from carbonic acid,  $\text{H}_2\text{CO}_3$  by removing  $\text{H}^+$  ions successively as follows:



## 6.2 Determination of Carbonates ( $\text{CO}_3^{2-}$ ) by Titrimetric Method

### 6.3 Principle of Measurement:

### 6.4 Alkalinity Testing:

Different alkalinity tests are all related to these significant pH's. Acid is added until a pH endpoint is achieved allowing the alkalinity components to be measured.

### 6.5 Phenolphthalein alkalinity:

Carbonates are present at pH greater than 8.3. Alkalinity due to carbonate is measured by using phenolphthalein. The P-alkalinity is a measure of the amount of acid required to drop the pH to approximately 8.3. As can be seen, this would measure the amount of any carbonate or hydroxide alkalinity present. Since the carbonate alkalinity is being converted to bicarbonate alkalinity, this test does not measure bicarbonate alkalinity.

Table 1: Existence of hydroxides, bicarbonate and carbonate at different pH

pH	10.2	OH <sup>-</sup>	CO <sub>3</sub> <sup>-2</sup>
	8.3	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>-2</sup>
	4.3	HCO <sub>3</sub> <sup>-</sup>	CO <sub>2</sub>
		Free Mineral Acidity & CO <sub>2</sub> (No significant alkalinity)	

### 6.6 Reagents:

- Hydrochloric Acid solution (0.1N)
- Hydrochloric Acid solution (0.02N)
- Sodium carbonate solution (0.05N))
- Phenolphthalein

### **6.6.1 Preparation of Phenolphthalein Indicator:**

#### **6.6.1.1 Reagents:**

- phenolphthalein
- Absolute Methanol

#### **6.6.1.2 Procedure:**

- Dissolve 0.8 g of phenolphthalein in 100mL absolute methanol.
- pH range is 8.3-10.0
- Color change from Pink to Colorless.

### **6.7 Standardization:**

For preparation and standardization of hydrochloric acid see Alkalinity UNIT 4

### **6.8 Procedure for analysis of sample:**

- To 10 mL sample 2 or 3 drops of phenolphthalein added pink color indication shows the pH range 8.3 or above.
- Titration is done against 0.02 N HCl
- Color changes from pink to transparent color.
- Alkalinity determined is called as Phenolphthalein Alkalinity as it gives color at pH 8.3.
- If pink color is indicated at pH less than 8.3, it shows the calibration error of pH meter.
- Numbers of replicates to be analyzed are “Three” for each sample.

### **6.9 Quality Control:**

- Method blank is analyzed after every 10 samples.
- WQL check repeatability by reanalyzing a pre-analyzed sample once a day
- Laboratory Control samples are analyzed with every batch of sample.

### **6.10 Expression of results:**

The carbonate is measured in mg/L.

Table 2: Alkalinity relationships

Result of Titration	Hydroxide Alkalinity as $\text{CaCO}_3$	Carbonate Alkalinity as $\text{CaCO}_3$	Bicarbonate Alkalinity as $\text{CaCO}_3$
$P = 0$	0	0	T
$P < \frac{1}{2} T$	0	2P	$T - 2P$
$P = \frac{1}{2} T$	0	2P	0
$P > \frac{1}{2} T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

Where P=phenolphthalein alkalinity, T=Total alkalinity

### 6.11 Safety precautions:

- Never smell and taste chemicals. Never pipette with mouth.
- Use chemical fume hood for preparation of reagents.
- Report damaged equipment or glassware to your supervisor.
- Do not eat or drink in the laboratory.

### 6.12 Checklist for testing of carbonates:

Sr no.	Checklist for testing	Yes/No
1.	Lab demonstration of carbonates testing	
2.	Glass ware washing	
2.	Preparation of Reagents and standards	
3.	Standardization of solutions	
4.	Perform testing	
5.	Result calculation	

### 6.13 Planned Demonstration:

Testing of carbonates in Chemical Lab-II (Reagents preparation, glassware washing, standards preparation, testing, quality control, calculations and reporting, units conversion).

#### **6.14 Class Exercises:**

- Surprise tests
- Analysis of unknown samples
- Quiz/Tutorials
- Lab demonstration test

#### **6.15 Group project:**

Water Quality Assessment

## Unit 7: Chloride

### 7 Chloride

#### 7.1 Introduction:

Chlorides are widely distributed in nature as salts of sodium (NaCl), potassium and calcium ( $\text{CaCl}_2$ ). It is one of the major anions in water and waste water. In potable water the salty taste produced by chloride concentration is variable and dependent on the chemical composition of water.

#### 7.2 Major uses:

Sodium chloride is widely used in the production of industrial chemicals such as caustic soda, chlorine, sodium chlorite, and sodium hypochlorite. Sodium chloride, calcium chloride, and magnesium chloride are extensively used in snow and ice control. Potassium chloride is used in the production of fertilizers. Chloride is a useful and reliable indicator of river/ground water fecal contamination, as chloride is a non-reactive solute and ubiquitous to sewage.

#### 7.3 Effects on humans;

Chloride is a chemical human body needs for metabolism (the process of turning food into energy). It also keeps the body's acid base balance. The amount of chloride in the blood is carefully controlled by the kidneys.

A normal adult human body contains approximately 81.7 g chloride. On the basis of a total obligatory loss of chloride of approximately 530 mg/day, a dietary intake for adults of 9 mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1 g of table salt per person per day). For children up to 18 years of age, a daily dietary intake of 45 mg of chloride should be sufficient. Chloride toxicity has not been observed in humans except in the special case of impaired sodium chloride metabolism, e.g. in congestive heart failure. Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a concomitant intake of fresh water. As in experimental animals, hypertension associated with sodium chloride intake appears to be related to the sodium rather than the chloride.

#### 7.4 Other effects:

- Chloride increases the electrical conductivity of water and thus increases its corrosivity.
- In metal pipes, chloride reacts with metal ions to form soluble salts, thus increasing levels of metals in drinking-water.

- In lead pipes, a protective oxide layer is built up, but chloride enhances galvanic corrosion. It can also increase the rate of pitting corrosion of metal pipes
- Chloride concentrations in excess of about 250 mg/litre can give rise to detectable taste in water, but the threshold depends upon the associated cations. Consumers can, however, become accustomed to concentrations in excess of 250 mg/L.

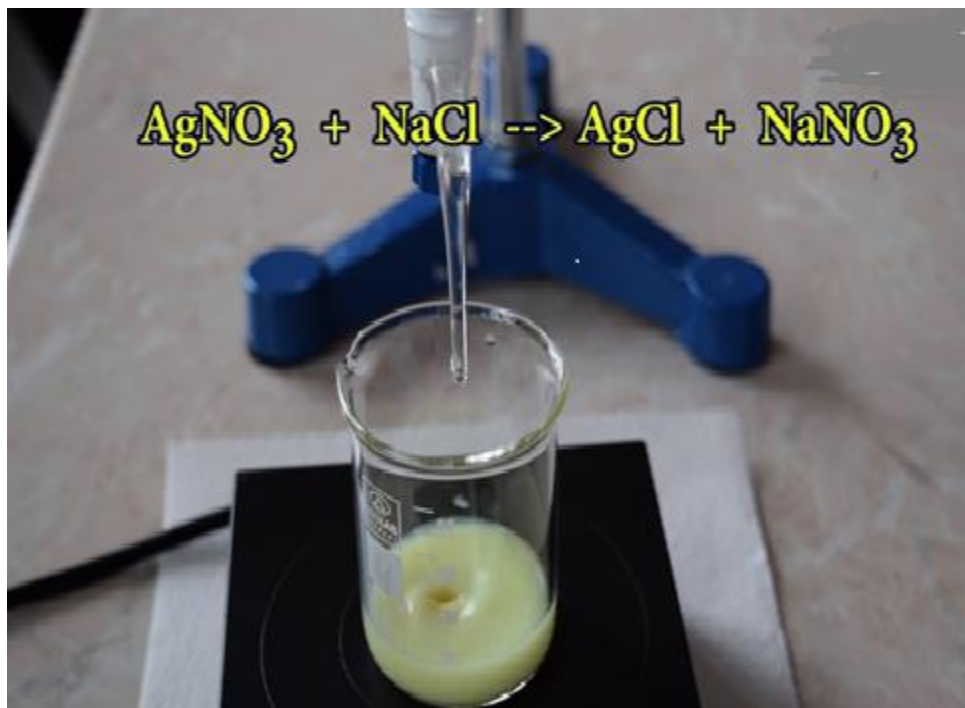
## 7.5 Treatment:

Chloride can be removed from drinking water by

- Distillation,
- Reverse osmosis (RO)
- Deionization (DI).
- Boiling, carbon adsorption filters and standard water softeners do not remove chloride.

## 7.6 Determination of Chlorides ( $\text{Cl}^{-1}$ ) by Argentometric Method:

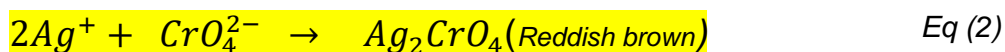
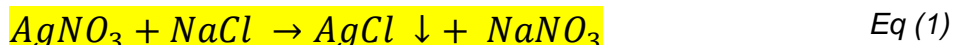
### 7.7 Principle of Measurement:



*Figure 7: Argentometric Titration Method*

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed represented in eq(1) and eq(2).

**Equation Representing overall reaction:**



## **7.8 Glassware:**

- Burette (0.05 mL)
- Pipette
- Glass beakers (100mL)
- Round bottom flask 1000 mL(amber colored)
- Round bottom flask 100 mL

## **7.9 Reagents:**

- Silver nitrate(0.0141N)
- Sodium chloride(0.0141N)
- Potassium Chromate Indicator

## **7.10 Preparation of Reagents:**

### **7.10.1 Preparation of 0.0141 N AgNO<sub>3</sub> solution:**

0.0141 N AgNO<sub>3</sub> solution is prepared by dissolving 2.3987 g of silver nitrate in 1000 mL of deionized water in amber colored 1000 mL flask.

### **7.10.2 Preparation of 0.0141N NaCl solution:**

0.0141N NaCl solution is prepared by dissolving 0.8281 g of NaCl in 1000 mL of deionized water in 1000 ml volumetric flask.

### **7.10.3 Potassium chromate indicator:**

5 g potassium chromate is dissolved in 100 mL deionized water.

## **7.11 Standardization of silver nitrate solution:**

### **7.11.1 Procedure of standardization:**

- Prepare 0.0141N Silver nitrate & 0.0141N sodium chloride solutions.
- Take 5 mL sodium chloride in a flask.



- Titrate 0.0141N Silver nitrate with the prepared 0.0141N sodium chloride using potassium chromate indicator.
- Carry out this procedure in triplicate.
- Calculate silver nitrate concentration.
- Adjust the strength of silver nitrate proportionally if necessary and re-titrate with sodium chloride.

### 7.12 Procedure for analysis of sample:

- To 20 mL Sample few drops of  $K_2CrO_4$  is added.
- It is titrated against 0.0141N  $AgNO_3$  with 25mL burette of 0.05mL resolution
- The burette reading is then noted when sample color changes to pinkish yellow.
- Number of replicates to be analyzed is “Three” for each sample.
- Method blank is analyzed after every 10 samples.

### 7.13 Calculation:

$$\text{mg Cl}^{-1}/\text{L} = \frac{(A - B) \times N \times 1000 \times 35.46}{\text{ml of sample}}$$

Where:

A = mL titration for sample

B = mL titration for blank

C = Normality of  $AgNO_3$

### 7.14 Expression of Results:

The chloride is measured in mg/L.

### 7.15 Quality Control:

- Method blank is analyzed after every 10 samples
- Laboratory Control samples of 16ppm and 100ppm analyzed with every batch of 10 samples.
- NWQL check repeatability by reanalyzing a pre-analyzed sample once a day

### 7.16 Safety precautions:

- Never smell and taste chemicals. Never pipette with mouth.
- Use chemical fume hood for preparation of reagents
- Report damaged equipment or glassware to your supervisor
- Do not eat or drink in the laboratory.

### 7.17 Checklist for testing of chlorides:

Sr no.	Checklist for testing	Yes/No
1.	Lab demonstration of chlorides testing	
2.	Glass ware washing	
2.	Preparation of Reagents and standards	
3.	Standardization of solutions	
4.	Perform testing	
5.	Result calculation	

### 7.18 Planned Demonstration:

Testing of chlorides in Chemical Lab-II (Reagents preparation, glassware washing, standards preparation, testing, quality control, calculations and reporting, units conversion)

### 7.19 Class Exercises:

- Surprise tests
- Analysis of unknown samples
- Quiz/Tutorials
- Lab demonstration test

### 7.20 Group project:

Water Quality Assessment