Experiment 8
Determination of Chloride in water



Introduction:

Chlorides occur in all natural waters in widely varying concentration, the chloride content normally increases as the mineral content increases. Upland and mountain supplies usually are quite low in chlorides, whereas river and groundwater usually have a considerable amount. Sea and ocean waters represent the residues resulting from partial evaporation of natural waters that flow into them and chloride levels are very high. Chlorides gain access to natural waters in many ways. The solvent power of water dissolves chlorides from topsoil and deeper formations. Spray from the ocean is carried inland as droplets or as minute salt crystals, which result from evaporation of the water in the droplets. These sources constantly replenish the chlorides in inland areas where they fall. Ocean and seawaters invade the rivers that drain into them, particularly the deeper rivers. The salt water, being denser, flows upstream under the fresh water, which is flowing downstream. There is a constant intermixing of the salt water with the fresh water above. Groundwater in areas adjacent to the ocean is in hydrostatic balance with seawater. Over-pumping of groundwater produces a difference in hydrostatic head in favor of the seawater, and it introduce into the fresh water area. Such intrusion has occurred in many areas of the coastal southern region of Bangladesh. Human excreta, particularly urine, contain chloride in an amount about equal to the chlorides consumed with food and water. This amount average about 6 gm of chlorides per person per day and increases the amount of CC in municipal wastewater about 15 mg/l above that of the carriage water. Thus, wastewater effluents add considerable chlorides to receiving streams. Many industrial wastes (e.g., tannery waste) also contain appreciable amount of chlorides.

Environmental significance:

Chlorides in reasonable concentrations are not harmful to human. At concentrations above 250 mg/L they give a salty taste to water, which is objectionable to many people. For this reason, chlorides are generally limited to 250 mg/L in supplies intended for public use. In many areas of the world where water supplies are scarce, source be containing as much as 2,000 mg/L are used for domestic purposes without the development of adverse effects, once the human system becomes adapted to the water.

Guideline:

According to Bangladesh Environment Conservation Rules (2023), drinking water standard for chloride is 250 mg/L; but for coastal regions of Bangladesh, the limit has been relaxed to 1000 mg/L.

Principle: (Mohr's Method)

This method determines the chloride ion concentration of a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a precipitate of silver chloride forms.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} \qquad \textbf{8.1}$$

The end point of the titration occurs when all the chloride ions are precipitated. Then additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

$$2Ag^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow Ag_2CrO_{4(s)} \qquad \textbf{8.2}$$

This method can be used to determine the chloride ion concentration of water samples from many sources such as seawater, stream water, river water and estuary water. The pH of the sample solutions should be between 6.5 and 10. If the solutions are acidic, the gravimetric method or Volhard's method should be used.

***The end point of titration cannot be detected visually unless an indicator capable of demonstrating the presence of excess Ag^+ is present. The indicator normally used is potassium chromate, which supplies chromate ions. As the concentration of CI^- ions becomes exhausted, the silver ion concentration increases and a reddish brown precipitate of silver chromate is formed.

$2Ag^+ + CrO_4^{2-} = Ag_2CrO_4$ **(reddish brown precipitate)** **8.3**

This is taken as evidence that all chloride has been precipitated. Since an excess Ag^+ is needed to produce a visible amount of Ag_2CrO_4, the indicator error is subtracted from all titrations.
The indicator error or blank varies somewhat with the ability of individuals to detect a noticeable color change. The usual range is 0.2 to 0.4 mL of titrant. An error of 0.2 mL will be used in the class.

Precautions:

1. A uniform sample size must be used, preferably 100 ml (or 50 mL), so that ionic concentrations needed to indicate the end point will be constant.
2. The pH must be in the range of 7 to 8 because Ag^+ is precipitated as AgOH at high pH levels and the CrO_4^{2-} is converted to $Cr_2O_7^{2-}$ at low pH levels,
3. A definite amount of indicator must be used to provide a certain concentration of CrO_4; otherwise Ag_2CrO_4 may form too soon or not soon enough.
4. The chromate solution needs to be prepared and used with care as chromate is a known carcinogen.
5. Silver nitrate solution causes staining of skin and fabric (chemical burns). Any spills should be rinsed with water immediately.

Apparatus:

1. Burette
2. Measuring cylinder
3. Beaker
4. Dropper
5. Stirrer

Reagents:

1. Potassium chromate indicator
2. Silver nitrate solution (0.0141 N)

Procedure:

1. Take 50 mL of the sample in a beaker and add 5 drops (about 1 mL) of potassium chromate indicator to it.
2. Add standard (0.0141 N) silver nitrate solution to the sample from a burette, a few drops at a time, with constant stirring until the first permanent reddish color appears. This can be determined by comparison with distilled water blank. Record the mL of silver nitrate used.
3. If more than 7 or 8 mL of silver nitrate solution are required, the entire procedure should be repeated using a smaller sample diluted to 50 ml with distilled water.

Calculation:

Chloride, Cl^- (mg/L)

= (mL of $AgNO_3$ used - "error" or "blank") x Multiplying Factor (M.F.)

Where, **M.F.** = $$\frac{\text{Normality of } AgNO_3 \text{ x equivalent wt. of } Cl^- \text{ x } 1000}{\text{ml of sample taken}}$$

Assignment

1. "Chlorides can introduce into natural waters in many ways" --explain.
2. Why it is necessary to dilute sample if end point does not obtained even after adding more than 7 or 8 mL silver nitrate to the original sample?
3. In determination of chloride, why an indicator "blank" or "error" is subtracted from the amount of silver nitrate used in titration? Explain.

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 $AgNO_3$ solution (mL)	Chloride Concentration (mg/L)
			Initial	Final		

Signature of the course teacher and date