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

# Experiment No. 8
# Determination of Chloride Concentration of Water

## INTRODUSTION

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 sea waters 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 the urine, contain chloride in an amount about equal to the chlorides consumed with flood and water. This amount average about 6 gm of chlorides per person per day and increases the amount of $Cl^-$ 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 IMPORTANCE

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 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. According to Bangladesh Environment Preservation Act (1997), drinking water standard for chloride is 150-600 mg/l; but for coastal regions of Bangladesh, the limit has been relaxed to 1000 mg/l.

Before the development of bacteriological testing procedures, chemical testes for chloride and for nitrogen, in its various forms, served as the basis of detecting contamination of

groundwater by wastewater. Chlorides are used to some extent as tracers in sanitary engineering practice; however, they have been replaced to a great extent by organic dyes.

## THEORY

Chlorides may be readily measured by means of volumetric procedures. For most purposes, the ***Mohr Method*** employing silver nitrate as the titrant and potassium chromate as the indicator is satisfactory. However, the procedure using mercuric nitrate and diphenylcarbazone as the indicator has certain inherent advantages over the *Mohr Method.*

*In Mohr* method the chloride of the sample in determined by titration with a standard silver nitrate solution in the presence of potassium chromate indicator. The "Standard Method" recommends a 0.0141 N silver nitrate solution which corresponds to a N/71 solution or a solution in which each milliliter is equivalent to 0.50 mg of chloride ion.

In the titration, chloride is precipitated as a white silver chloride (Eq. 1)

$$Ag^+ + Cl^- = AgCl \text{ (white precipitate)} \qquad (1)$$

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 in potassium chromate, which supplies chromate ions. As the concentration of $Cl^-$ ions becomes exhausted, the silver ion concentration increases and a reddish brown precipitate of silver chromate is formed (Eq. 2).

$$2Ag^+ + CrO_4^{2-} = Ag_2CrO_4 \text{ (reddish brown precipitate)} \qquad (2)$$

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.

Several precautions must be observed in determination of chloride for ensuring accuracy:

(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 then $CrO_4^{2-}$ 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 $CrO_4^{2-}$, otherwise $Ag_2CrO_4$ may form too soon or not soon enough.

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 this class.

## REAGENTS

(1) Potassium chromate indicator
(2) Silver nitrate solution (0.0 141N)

## APPARATUS

| | |
|---|---|
| (1) Measuring cylinder (100 ml) | : 1 pc. |
| (2) Beaker | : 1 pc. |
| (3) Dropper | : 1 pc. |
| (4) Stirrer | : 1 pc. |

## 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") × Multiplying Factor (MF)

where, MF= normality of $AgNO_3$ × equivalent wt. of $Cl^-$ × 1000 / (milliliter of sample taken)

## ASSIGNMENT QUESTIONS

(1) Discuss the environmental significance of chloride in water.

(2) What precautions should be taken in the determination of chloride concentration by Mohr method? Explain why.

(3) In determination of chloride, why an indicator "blank" or "error" is subtracted from the amount of silver nitrate used in titration? Explain.