EXPERIMENT NO:- 4

Aim: To determine chloride ion in a given water sample by argentometric method

Theory:

Chlorides are present in water usually as NaCl, $MgCl_2$ and $CaCl_2$. Although chlorides are not harmful as such, their concentration above 250 ppm imparts a peculiar taste to the water thus rendering the water unacceptable for drinking purpose. Further existence of unusually high concentrations of chloride in a water sample indicates pollution from domestic sewage or from industrial waste water. Salts like $MgCl_2$ may undergo hydrolysis under the high pressure and temperature prevailing in the boiler, generating hydrochloric acid which causes corrosion in boiler parts. Chlorides in the form of $MgCl_2$ and $CaCl_2$ cause permanent hardness and are a source of trouble not only at our house hold but also in industries.
By Argentometric method, estimation of chlorides in a water sample can be quantitatively carried out in a neutral medium, since silver hydroxide gets precipitated in alkaline medium leading to erroneous results and in acidic medium some chromate is converted to dichromate.

$$Ag^+ + OH^- = AgOH \;;\quad 2CrO_4^{2-} + 2H^+ \rightarrow 2HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O$$

When silver nitrate is added to a solution of sodium chloride containing potassium chromate, Ag^+ first reacts with Cl^- to give a white precipitate of AgCl and not Ag_2CrO_4.

$$Ag^+ + Cl^- \longrightarrow AgCl \text{ (white precipitate)} \qquad (K_{SP1} = 1.2 \times 10^{-10})$$

$$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4 \text{ (Red precipitate)} \qquad (K_{SP2} = 1.7 \times 10^{-12})$$

Where the K_{sp} values in parenthesis indicate their respective solubility products (the greatest possible value of ionic product for a saturated solution, beyond which precipitation occurs).
If the solubility of the solids is indicated by S_1 and S_2

Then, $K_{SP1} = S_1 \times S_1$ or, $S_1^2 = K_{SP1}$ or, $S_1 = \sqrt{K_{SP1}} = 1.732 \times 10^{-5}$

$K_{SP2} = (2S_2)^2 \times S_2$ or, $4S_2^3 = K_{SP2}$ or, $S_2 = (K_{SP2}/4)^{1/3} = 1.076 \times 10^{-4}$

Thus solubility of Ag_2CrO_4 being more than that of AgCl, the former will start to precipitate after complete precipitation of later. So, during the titration the solution will be turbid due to appearance of AgCl and the equivalence point of the precipitation titration is indicated by the appearance of red color (Ag_2CrO_4) from yellow color (K_2CrO_4). From this titre value concentration of total chloride can be calculated.

Apparatus and Reagents:

- Burette
- Pipette (10ml and 25ml)
- Conical flask (100ml)
- Beaker (100ml)
- Funnel

primary standard sodium chloride solution
secondary standard silver nitrate solution
potassium chromate indicator
water sample

Procedure:

Step-1: Standard (~ N/50) sodium chloride solution and silver nitrate solution is provided

Step-2: Standardization of silver nitrate solution
Pipette out 10 ml of (~ N/50) sodium chloride solution in a 100 ml conical flask, add 4-5 drops of potassium chromate indicator into it and titrate the resulting solution with (~ N/50) silver nitrate solution taken in burette. Add drop wise silver nitrate solution from burette until yellow color start changing to brown red colour. The titration is repeated two times to get a concordant reading.

Step-3: Estimation of chloride content
Pipette out 25 ml water sample in a 100 ml conical flask, add 4-5 drops of potassium chromate indicator into it and titrate the resulting solution with
(~ N/50) silver nitrate solution taken in burette. Add drop wise silver nitrate solution from burette until yellow colour start changing to brown red colour. The titration is repeated two times to get a concordant reading.

Result and Calculations:

Table-1: Standardization of silver nitrate solution

Strength of sodium chloride solution (S_1) = ... (N)

No of observation	Volume of sodium chloride solution (V_1 ml)	Burette Reading		Volume of $AgNO_3$ required (ml)	Mean volume of $AgNO_3$ required (V_2 ml)
		Initial (ml)	Final (ml)		
1	10				
2	10				
3	10				

We know, $V_1S_1 = V_2S_2$

$S_2 = V_1S_1 / V_2$ (N)

Table-2: Estimation of chloride content:

Strength of $AgNO_3$ (S_2) = ... (N)

No of observation	Volume of Water sample taken (ml)	Burette Reading		Volume of $AgNO_3$ required (ml)	Mean volume of $AgNO_3$ required (V')ml
		Initial (ml)	Final (ml)		
1	25				
2	25				
3	25				

1000 ml 1 (N) $AgNO_3 \equiv 35.5$ gm of chloride ion

$V' \text{ ml } S_2 \text{ (N) } AgNO_3 \equiv (35.5 \times V' \times S_2) / 1000$ gm of chloride ion

$= x$ gm of chloride ion

Now, 25 ml water sample contains x gm of chloride ion

$\therefore 10^6$ ml of water sample contains $(x \times 10^6) / 25$ gm of chloride ion

$\therefore$ Chloride content in the given water sample = $(x \times 10^6) / 25$ ppm

Precaution:

i. Before starting of the experiment the whole apparatus should be washed with distilled water which is free of chlorine.
ii. Carefully handle silver nitrate and avoid any skin contact since silver nitrate is corrosive and leaves blacks spots.
iii. Add same amount of indicator each time.

Conclusion:

The chloride content in a given water sample is =............. ppm