

PRECIPITATION TITRIMETRY

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Precipitation titrimetry

which is based on reactions that yield ionic compounds of limited solubility. Because of the slow rate of formation of most precipitates, however, there are only a few precipitating agents that can be used in titrimetry.

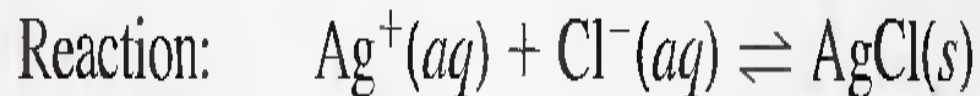
the most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions (SCN^- , CN^- , CNO^-), mercaptan, fatty acids, and several divalent and trivalent inorganic anions.

Titrimetric methods based on silver nitrate are sometimes called argentometric methods.

Precipitation Titration Curves Involving Silver Ion:

A titration curve for this method usually consists of a plot of pAg versus the volume of silver nitrate added.

EXAMPLE 13-10 : Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃ (for AgCl, $K_{sp} = 1.82 \times 10^{-10}$). (a) after added 10 mL of AgNO₃ (b) at equivalence point. (c) after added 26.00 mL of the reagent.



(1) Preequivalence-Point Data

Here the molar analytical concentration c_{NaCl} is readily computed. For example, when 10.00 mL of AgNO_3 has been added,

$$c_{\text{NaCl}} = \frac{\text{original number of mmol NaCl} - \text{no. mmol AgNO}_3 \text{ added}}{\text{total volume solution}}$$

But

$$\text{original number of mmol NaCl} = 50.00 \text{ mL} \times 0.0500 \frac{\text{mmol NaCl}}{\text{mL}} = 2.500$$

$$\text{number of mmol AgNO}_3 \text{ added} = 10.00 \text{ mL} \times 0.1000 \frac{\text{mmol AgNO}_3}{\text{mL}} = 1.000$$

$$\text{no. mmol NaCl remaining} = 1.500$$

$$c_{\text{NaCl}} = \frac{1.500 \text{ mmol NaCl}}{(50.00 + 10.00) \text{ mL}} = 0.02500 \frac{\text{mmol NaCl}}{\text{mL}} = 0.02500 \text{ M}$$

$$[\text{Cl}^-] = 0.02500 \text{ M}$$

$$[\text{Ag}^+] = K_{\text{sp}} / [\text{Cl}^-] = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9} \text{ M}$$

$$\text{pAg} = -\log (7.28 \times 10^{-9}) = 8.14$$

(2) Equivalence Point pAg

Here,

$$[\text{Ag}^+] = [\text{Cl}^-] \quad \text{and} \quad [\text{Ag}^+][\text{Cl}^-] = 1.82 \times 10^{-10} = [\text{Ag}^+]^2$$

$$[\text{Ag}^+] = 1.349 \times 10^{-5} \text{ M} \quad \text{and} \quad \text{pAg} = -\log(1.349 \times 10^{-5}) = 4.87$$

(3) Postequivalence-Point Data

At 26.00 mL AgNO_3 added, Ag^+ is in excess, so

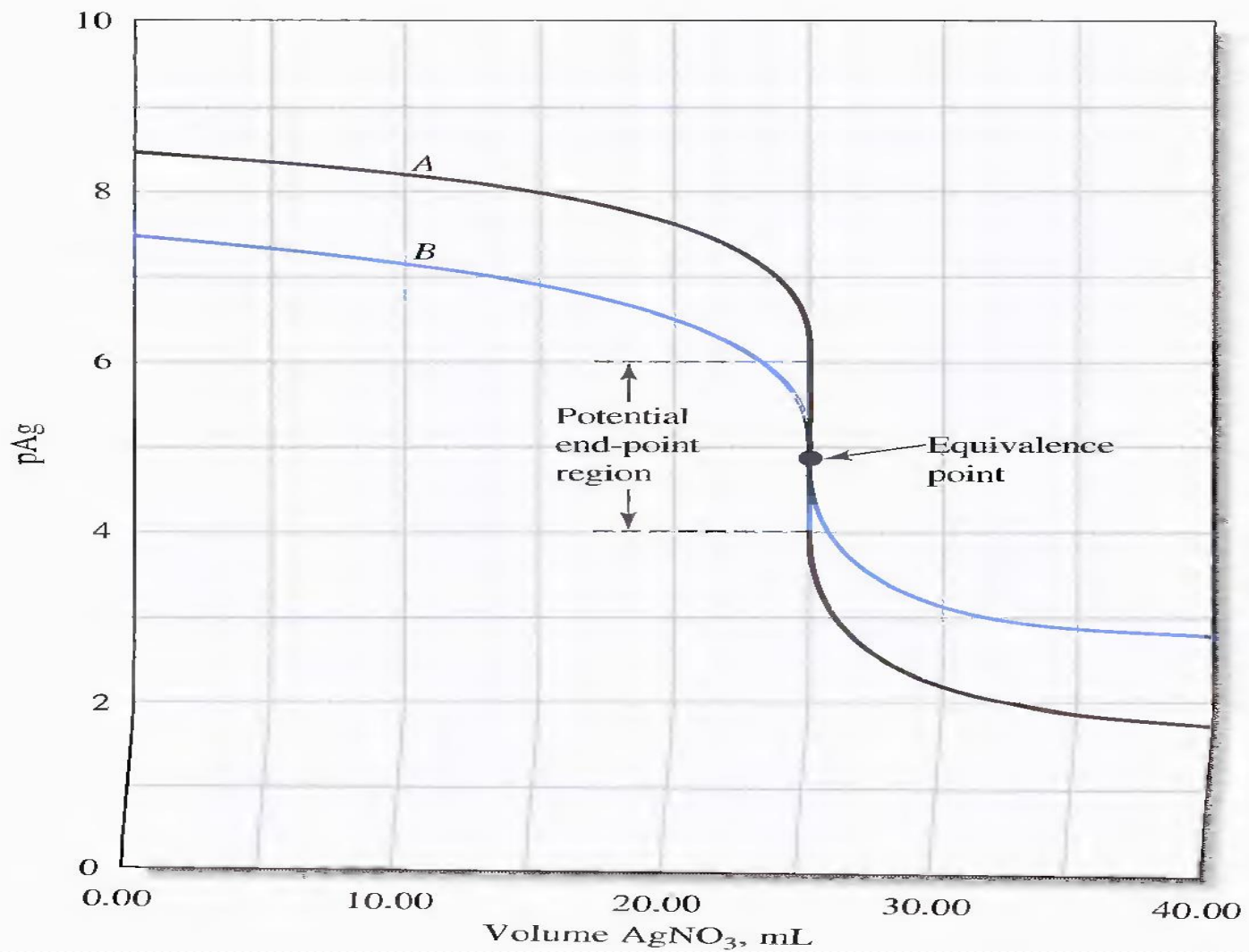
$$[\text{Ag}^+] = c_{\text{AgNO}_3} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{50.00 - 26.00} = 1.316 \times 10^{-3} \text{ M}$$

$$\text{pAg} = -\log(1.316 \times 10^{-3}) = 2.88$$

TABLE 13-2**Changes in pAg in the Titration of Cl⁻ With Standard AgNO₃**

Volume of AgNO ₃	pAg	
	50.00 mL of 0.0500 M NaCl	50.00 mL of 0.00500 M NaCl
	with 0.1000 M AgNO ₃	with 0.01000 M AgNO ₃
10.00	8.14	7.14
20.00	7.59	6.59
24.00	6.87	5.87
25.00	4.87	4.87
26.00	2.88	3.88
30.00	2.20	3.20
40.00	1.78	2.78

Figure 13-4 Titration curve for *A*, 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃, and *B*, 50.00 mL of 0.00500 M NaCl with 0.0100 M AgNO₃.



The Effect of Concentration on Titration Curves

the two titration curves in Figure 13-4. With 0.1 M AgNO_3 (Curve A), the change in pAg in the equivalence-point region is large.

With the 0.01 M reagent, the change is markedly less but still pronounced.

Thus, an indicator for Ag^+ that produces a signal in the 4.0 to 6.0 pAg range should give a minimum error for the stronger solution. For the more dilute chloride solution, the change in pAg in the equivalence-point region would be too small to be detected precisely with a visual indicator.

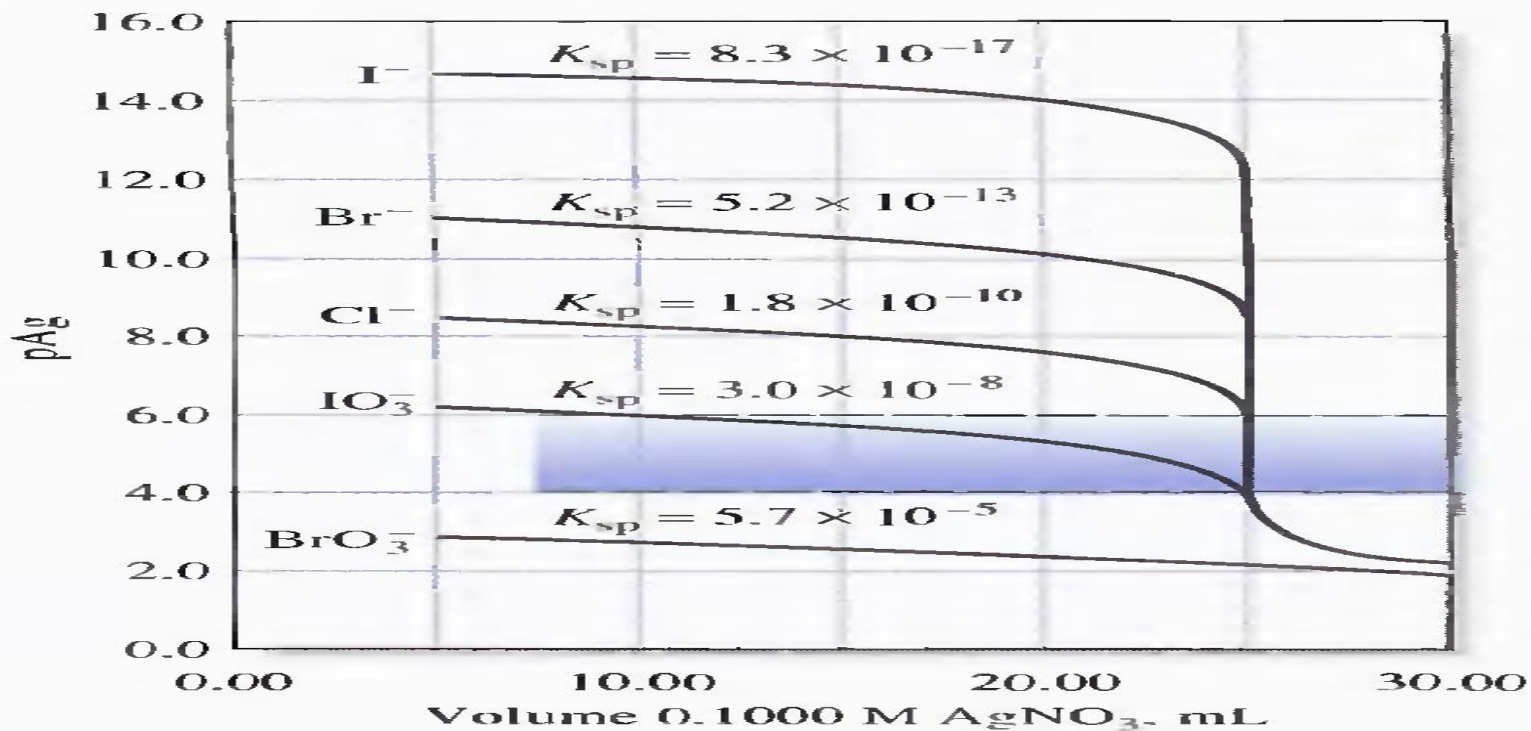


Figure 13-5 illustrates the effect of solubility product on the sharpness of the end point in titrations with 0.1 M silver nitrate. Clearly, the change in pAg at the equivalence point becomes greater as the solubility products become smaller, that is, as the reaction between the analyte and silver nitrate becomes more complete. By careful choice of indicator—one that changes color in the region of pAg from 4 to 6—titration of chloride ion should be possible with a minimal titration error.

Indicators for Argentometric Titrations:

Two types of indicators are employed:

○The 1st type forms a colored compound with the titrant when it is in excess.

○The 2nd type called the adsorption indicator, suddenly becomes adsorbed on the precipitate at the equivalence point.

Chemical indicator:

The end point produced by a chemical indicator usually consists of a color change or, occasionally, the appearance or disappearance of turbidity in the solution being titrated. The requirements for an indicator for a precipitation titration are that

(1) the color change should occur over a limited range in p-function of the reagent or the analyte .a

(2) the color change should take place within the steep portion of the titration curve for the analyte.

Chemical Indicators

Precipitation Type - Mohr's method

Adsorption – Fajan's method

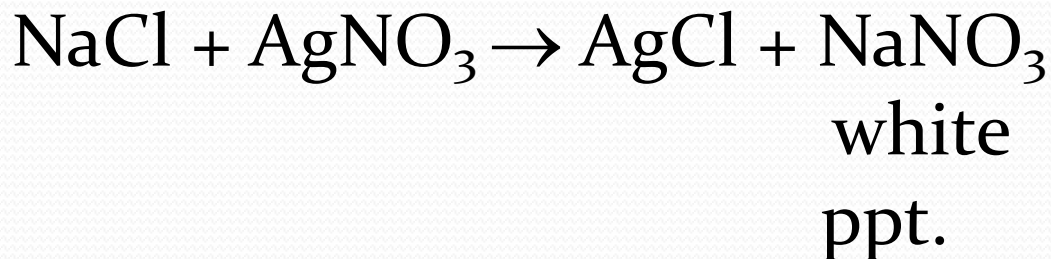
For silver analyses –Volhard method

1. Indicators reacting with the titrant

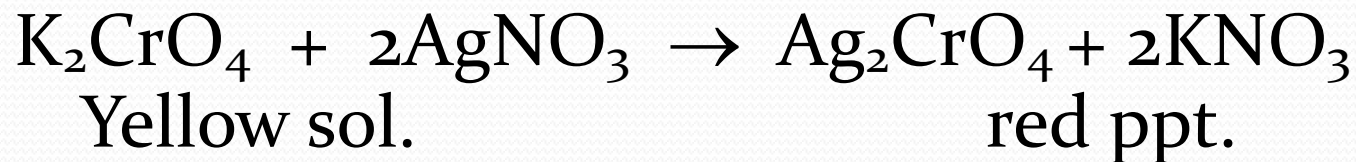
(a)The Mohr Method (using sodium chromate as indicator): Mohr method for determination of chloride in some sample. the titration reaction is

(a) Mohr method:

The Cl^- is titrated with std. AgNO_3 solution.



A soluble CrO_4^{2-} salt is added as the indicator. This produces a yellow solution. When the precipitation of Cl^- is complete, the first excess of Ag^+ reacts with the indicator to precipitate red silver chromate.



1- Sodium chromate can serve as an indicator for the argentometric determination of chloride, bromide, and cyanide ions by reacting with silver ion to form a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region.

2- The silver ion concentration at chemical equivalence in the titration of chloride with silver ions is given by

$$[\text{Ag}^+] = \sqrt{K_{\text{sp}}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5} \text{ M}$$

3- The chromate ion concentration required to initiate formation of silver chromate under this condition can be computed from the solubility constant for silver chromate,

$$[\text{CrO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ag}^+]^2} = \frac{1.2 \times 10^{-12}}{(1.35 \times 10^{-5})^2} = 6.6 \times 10^{-3} \text{ M}$$

4- chromate ion and silver ion should be added in amount to give clear red precipitate ,the two concentration above is too low to appear sharp color, and these two factors create a positive systematic error in the Mohr method, and this corrected using calcium carbonate.

5- The Mohr titration must be carried out at a pH of 7 to 10 because chromate ion is the conjugate base of the weak chromic acid. Consequently, in more acidic solutions, the chromate ion concentration is too low to produce the precipitate near the equivalence point. While at basic medium Ag will precipitate as $\text{Ag}(\text{OH})$, Normally, a suitable pH is achieved by saturating the analyte solution with sodium hydrogen carbonate.

(b)The Fajans Method (using adsorption Indicators):

1-The indicator reaction takes place on the surface of the precipitate. The indicator, which is a dye exist in solution as the ionized form, usually an anion, In^- .

2-e.g. titration of Cl^- with Ag^+ Before eq. point, Cl^- is in excess and the 1ry adsorbed layer is Cl^- . The 2ry adsorbed layer (counter) is cation.



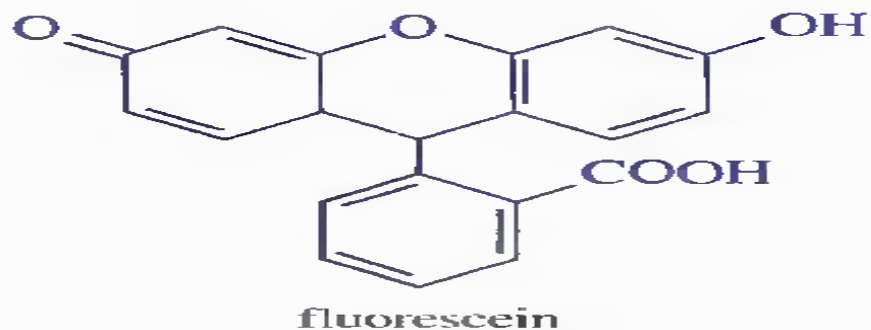
3- Beyond eq. point, Ag^+ is in excess with the 1ry layer being Ag^+ . This will attract the indicator anion and adsorb it in the counter layer.



4- The color of the adsorbed indicator is different from that of the unadsorbed indicator, and this difference signals the completion of the titration.

5- These indicators are usually weak acids, and if the pH is too low (highly acidic) they will not strongly adsorb on the ppt. If the indicator is a stronger acid, it can be adsorbed over a wide pH range.

e.g. Fluorescein, Eosin



6- Also, the indicator must not be too strongly adsorbed, or it will displace the anion of the precipitate in the 1ry layer before the eq. point is reached.

7- The degree of adsorption of the indicator can be decreased by increasing the acidity.

(c)The Volhard Method(using Iron(III) Ion as indicator):

It is an indirect titration for determining anions that precipitate with Ag^+ (Cl^- , Br^- , SCN^-), and performed in acid solution (HNO_3).

A measured excess of AgNO_3 is added to precipitate the anions, and the excess Ag^+ is determined by back-titration with standard SCN^- solution.

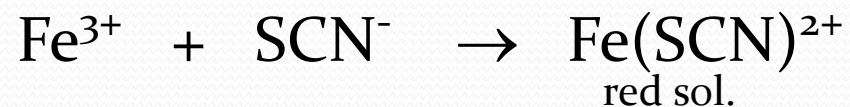


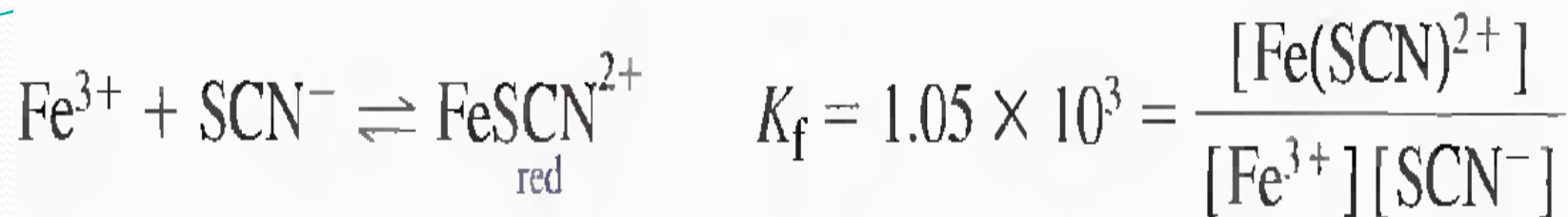
Yellow ppt.



White ppt.

The end point is detected by adding iron (III) as a ferric alum (ferric ammonium sulfate), which forms a soluble red complex with the first excess of titrant.





► Volhard method for chloride.



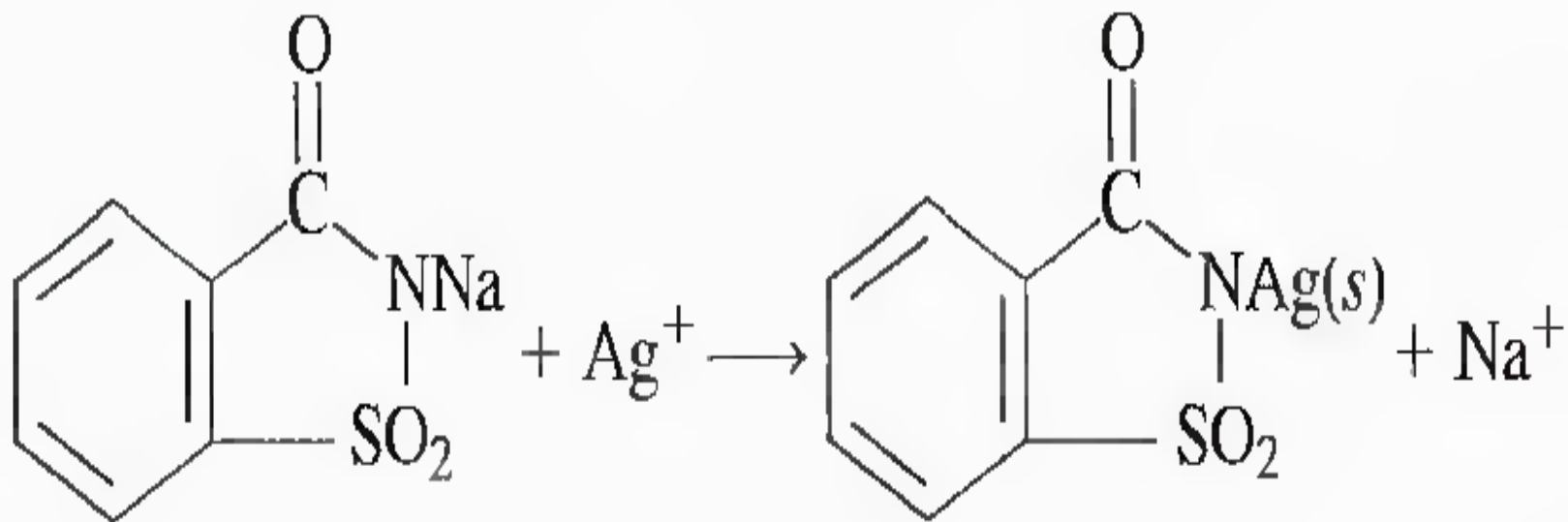
Notes

- 1-The titration must be carried out in acidic solution to prevent precipitation of iron(III) as the hydrated oxide,
- 2- also such ions as carbonate ,oxalate ,and arsenate(which form soluble silver salts in neutral media but not in acidic media) do not interfere.
- 3- In practice, an indicator concentration greater than 0.2M imparts sufficient color to the solution to make detection of the thiocyanate complex difficult because of the yellow color of Fe^{3+} . Therefore, lower concentrations (usually about 0.01 M) of iron(III) ion are employed.

The most important application of the Volhard method is the indirect determination of halide ions. A measured excess of standard silver nitrate solution is added to the sample, and the excess silver is determined by back-titration with a standard thiocyanate solution.

Problems:

***13-23.** A 20-tablet sample of soluble saccharin was treated with 20.00 mL of 0.08181 M AgNO_3 . After removal of the solid, titration of the filtrate and washings required 2.81 mL of 0.04124 M KSCN. Calculate the average number of milligrams of saccharin (205.17 g/mol) in each tablet. The reaction is



Solution:

$$V_{\text{KSCN}} \times N_{\text{KSCN}} = V_{\text{AgNO}_3} \times N_{\text{AgNO}_3}$$

$$2.81 \times 0.04124 = V_{\text{AgNO}_3} \times 0.08181$$

$$V_{\text{AgNO}_3} = 1.417 \text{ mL this is excess of AgNO}_3.$$

The volume of AgNO_3 that reacted with drug.

$$V_{\text{AgNO}_3} = 20.00 - 1.417 = 18.58 \text{ mL}$$

$$V_{\text{AgNO}_3} \times N_{\text{AgNO}_3} = (\text{wt} / \text{Mt}) \times 1000$$

$$18.58 \times 0.08181 = (\text{Wt} / 205.17) \times 1000$$

$$\text{Wt} = 0.312 \text{ g} \quad \text{Wt} = 312 \text{ mg} / 20 = 15.59 \text{ mg}$$

Problem 2:

A 0.435g sample of chloride ion Titrated using Mohr method required 36.8mL of 0.106 N AgNO_3 . Calculate the % of chloride in the sample.



Solution :

n.of meq Ag^+ = n.of meq of Cl^- at
equivalence point .

$$V_{\text{AgNO}_3} \times N_{\text{AgNO}_3} = (\text{wt} / \text{eq}_{\text{wt}}) \times 1000$$

$$36.8 \times 0.106 = (\text{Wt}/35.5) \times 1000$$

$$\text{Wt} = 0.1385 \text{ g}$$

$$\% \text{ of } \text{Cl}^- = (0.1385 / 0.435) \times 100 = 31.8 \%$$



Thank You