

13 Titrimetric Methods; Precipitation Titrimetry

Titrimetric method: analytical procedures in which the amount of analyte is determined from the amount of a standard reagent required to react with the analyte completely.

Three types of quantitative titrimetry

1. volumetric (the most widely used)
2. gravimetric
3. coulometric

13A Some Terms Used in Volumetric Titrimetry

***Standard solution** (standard titrant)

1. accurate known conc. : 4 significant figures
2. stable
3. stoichiometric reaction : whole-number ratio
4. rapid and quantitatively complete reaction : 99.9 %

***Titration**

***Direct titration**

***Back-titration, residual-titration:** when the rate of reaction between the analyte and reagent is slow or when the reagent lacks stability.

***Equivalence point**, theoretical point: the point in a titration when the amount of added standard reagent exactly equivalent to the amount of analyte.

***End point:** the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

***Titration error E_t :** the difference in volume or mass between the equivalence point and the end point. ($V_{ep} - V_{eq}$)

***Indicator:** large changes in the relative conc. of analyte or titrant occur in the equivalence-point region.

- a. appearance or disappearance of a color.
- b. change in color
- c. appearance or disappearance of turbidity.

Instruments for detect end point: voltmeters, ammeters, ohmmeters, colorimeters, temperature recorders, refractometers.



Fig. 13-1 The titration process

***Primary standards:**

1. high purity
2. stability in air
3. absence of hydrate water
4. ready availability at modest cost
5. reasonable solubility in the titration medium
6. reasonably large formula weight

***Secondary standard**

13B Standard Solutions

***Standardization, establishing the conc. of standard soln.**

1. Direct method: carefully weighed quantity of a primary standard
 → dissolved → diluted to an exactly known volume.
2. Standardized by titrating

a. a weighed quantity of a primary standard	
b. a weighed quantity of a secondary standard	secondary standard solution
c. a measured volume of another standard soln	

***Methods for expressing the conc. of standard solutions**

- a. molarity C : no. of moles/L soln
- b. normality C_N : no. of equivalent/L soln.

13C Volumetric calculations

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} = V(\text{L}) \times C_A \left(\frac{\text{mol}}{\text{L}} \right)$$

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mmol)}} = V(\text{mL}) \times C_A \left(\frac{\text{mmol}}{\text{mL}} \right)$$

***Calculation of the Molarity of Standard Solutions (SS)**

Ex. 13-1. Describe the preparation of 2.000 L of 0.0500 M AgNO₃ (169.87 g/mol) from the primary standard-grade solid.

$$\text{amount AgNO}_3 = 0.050 \text{ L} \times 2.000 \text{ mol/L} = 0.1000 \text{ mol}$$

$$\text{mass AgNO}_3 = 0.1000 \text{ mol} \times 169.87 \text{ g/mol} = 16.98 \text{ g}$$

dissolving 16.98 g AgNO₃ in water and diluting to 2.000 L.

Ex. 13-2. Describe how 500 mL of standard 0.0100 M Na⁺ solution can be prepared from primary standard Na₂CO₃(105.99 g/mol).

$$\text{amount Na}_2\text{CO}_3 = 500 \text{ mL} \times 0.0100 \text{ mmol/mL} \times \frac{1}{2} = 2.50 \text{ mmol}$$

$$\text{mass Na}_2\text{CO}_3 = 2.50 \text{ mmol} \times 0.10599 \text{ g/mmol} = 0.265 \text{ g}$$

→ dissolving 0.265 g Na₂CO₃ in water and diluting to 500 mL.

Ex. 13-3. How would you prepare 50.0-mL portions of SS that are 0.00500 M, 0.00200 M and 0.00100 M in Na⁺ from the soln in Ex. 2?

$$V_{\text{concd}} \times C_{\text{concd}} = V_{\text{dil}} \times C_{\text{dil}}$$

$$V_{\text{concd}} = \frac{V_{\text{dil}} \times C_{\text{dil}}}{C_{\text{concd}}} = \frac{50.0 \text{ mL} \times 0.00500 \text{ mmol Na}^+ / \text{mL}}{0.0100 \text{ mmol Na}^+ / \text{mL}} = 25.0 \text{ mL}$$

	0.00500M	0.00200M	0.00100M
0.0100 M Na ⁺ soln	25.0 mL	10.0 mL	5.00 mL

Ex. 13-4. Describe how you would prepare 2.0 L of approximate 0.25 M HClO₄ (100.46 g/mol) from the conc. reagent, which has a specific gravity of 1.67 g/mL and contains 71 % (w/w) HClO₄.

$$C_{\text{HClO}_4} = 1.67 \text{ (g/mL)} / 0.10046 \text{ (g/mmol)} \times 0.71 = 11.8 \text{ M}$$

$$\text{no. mmol HClO}_4 \text{ required} = 2000 \text{ mL} \times 0.25 \text{ mmol/mL} = 500 \text{ mmol}$$

$$\text{vol conc. reagent} = 500 \text{ mmol} / 11.8 \text{ (mmol/mL)} = 42.4 \text{ conc. reagent}$$

→ diluted about 42 mL of 71 % HClO₄ to 2.0 L.

***Calculation of Molarities from Standardization Data**

Ex. 13-5. A 50.00-mL of an HCl solution required 29.71 mL of 0.01963 M Ba(OH)₂ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl. Ba(OH)₂ + 2HCl → BaCl₂ + 2H₂O

1 mmol Ba(OH)₂ reacts with 2 mmol of HCl

$$\text{amount Ba(OH)}_2 = 29.71 \text{ mL} \times 0.01963 \text{ mmol/mL} = 0.5832 \text{ mmol}$$

$$\text{amount HCl} = 2 \times 0.5832 = 1.1664 \text{ mmol}$$

$$C_{\text{HCl}} = \frac{(29.71 \times 0.01963 \times 2) \text{ mmol HCl}}{50.0 \text{ mL soln}} = 0.023328 \text{ M} = 0.0233 \text{ M}$$

Ex. 13-6. Titration of 0.2121 g pure $\text{Na}_2\text{C}_2\text{O}_4$ (134.00 g/mol) required 43.31 mL KMnO_4 . What is the molarity of the KMnO_4 soln?



$$\text{stoichiometric ratio} = \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}$$

$$\text{amount Na}_2\text{C}_2\text{O}_4 = \frac{0.2121 \text{ g}}{0.13400 \text{ g/ mmol}}$$

$$\text{amount KMnO}_4 = \frac{0.2121}{0.13400} \text{ mmol} \times \frac{2}{5}$$

$$C_{\text{KMnO}_4} = \frac{\left(\frac{0.2121}{0.1340} \times \frac{2}{5}\right) \text{ mmol}}{43.31 \text{ mL}} = 0.01462 \text{ M}$$

*Calculation the Quantity of Analyte from Titration Data

Ex. 13-7. A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{2+} and titrated with 47.22 mL of 0.02242 M KMnO_4 solution. Calculate the results of this analysis in term of (a) % Fe (55.847 g/mol); and (b) % Fe_3O_4 (231.54 g/mol).



$$\text{(a). stoichiometric ratio} = \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$$

$$\text{amount KMnO}_4 = 47.22 \text{ mL} \times 0.02242 \text{ mol/L} = 1.0587 \text{ mmol}$$

$$\text{amount Fe}^{2+} = 47.22 \text{ mL} \times 0.02242 \text{ mol/L} \times 5 = 5.2934 \text{ mmol}$$

$$\text{mass Fe}^{2+} = 5.2934 \text{ mmol} \times 0.055847 \text{ g/mmol} = 0.2956 \text{ g}$$

$$\text{percent Fe}^{2+} = \frac{(47.22 \times 0.02242 \times 5 \times 0.055847) \text{ g}}{0.8040 \text{ g sample}} \times 100\% = 36.77\%$$

$$\text{(b). stoichiometric ratio:} = 5 \text{ Fe}^{2+} \equiv 1 \text{ MnO}_4^-$$

$$5 \text{ Fe}_3\text{O}_4 \equiv 15 \text{ Fe}^{2+} \equiv 3 \text{ MnO}_4^-$$

$$\text{amount KMnO}_4 = 47.22 \text{ mL} \times 0.02242 \text{ mol/L} = 1.0587 \text{ mmol}$$

$$\text{amount Fe}_3\text{O}_4 = 47.22 \text{ mL} \times 0.02242 \text{ mol/L} \times \frac{5}{3} = 1.76445 \text{ mmol}$$

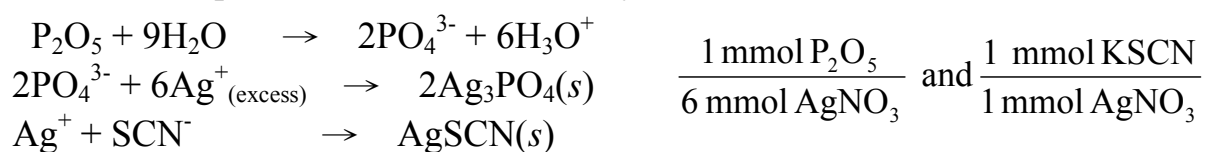
$$\text{mass Fe}_3\text{O}_4 = 1.76445 \text{ mmol} \times 0.23154 \text{ g/mmol} = 0.4085 \text{ g}$$

$$\text{percent Fe}_3\text{O}_4 = \frac{(47.22 \times 0.02242 \times \frac{5}{3}) \times 0.23154 \text{ g}}{0.8040 \text{ g sample}} \times 100\% = 50.81\%$$

Ex.13-8. A 100.0-mL sample of brackish water was made ammonical, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M AgNO₃. The analytical reaction is 2Ag⁺ + S²⁻ → Ag₂S(s) Calculate [H₂S] in the water in ppm.

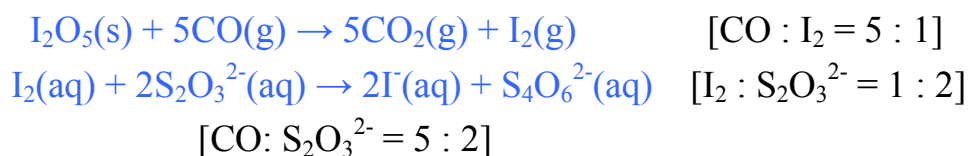
$$[\text{H}_2\text{S}] = \frac{(16.47 \times 0.02310 \times \frac{1}{2}) \times 0.034802\text{g}}{100.0 \text{ mL} \times 1.000\text{g/mL sample}} \times 10^6 \text{ ppm} = 66.2 \text{ ppm H}_2\text{S}$$

Ex. 13-9. The phosphorus in a 4.258-g sample of a plant food was converted to PO₄³⁻ and precipitated as Ag₃PO₄ through the addition of 50.00 mL of 0.0820 M AgNO₃. The excess AgNO₃ was back-titrated with 4.06 mL of 0.0625 M KSCN. Express the results of the analysis in terms of % P₂O₅.



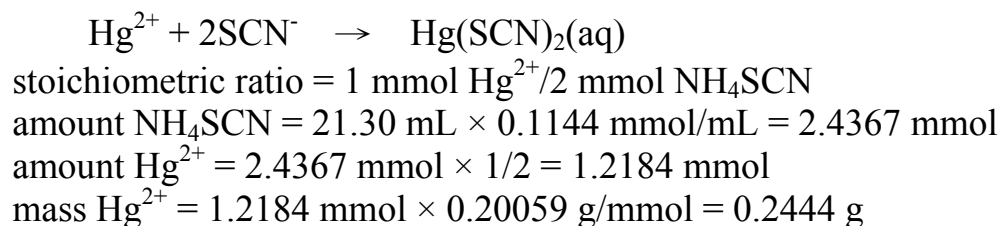
$$\% \text{P}_2\text{O}_5 = \frac{(50.00 \times 0.0820 - 4.06 \times 0.0625) \times \frac{1}{6} \times 0.1419\text{g/mmol}}{4.258 \text{ g sample}} \times 100\% = 2.14\%$$

Ex. 13-10 The CO in a 20.3-L sample of gas was converted to CO₂ by passing the gas over iodine pentoxide heated to 150°C, and I₂ was distilled and collected to 8.25 mL of 0.01101 M Na₂S₂O₃, then back titration with 2.16 mL of 0.00947 M I₂ solution. Calculate the mg of CO (28.01 g/mol) per liter of sample.



$$\begin{aligned} \text{Mass CO} &= \frac{(8.25 \times 0.01101 - 2.16 \times 0.00947 \times 2) \times \frac{5}{2} \times 28.01}{20.3 \text{ L}} \\ &= \frac{0.1248 \text{ mmol} \times 28.01}{20.3} = \frac{3.4956}{20.3} = 0.172 \text{ mg/L} \end{aligned}$$

Ex. 11 The organic matter in a 3.776-g sample of a mercuric ointment is decomposed with HNO₃. After dilution, the Hg²⁺ is titrated with 21.30 mL of a 0.1144 M soln of NH₄SCN. Calculate the percent Hg (200.59 g/mol) in the ointment.



$$\text{percent Hg} = \frac{(21.30 \times 0.1144 \times \frac{1}{2}) \times 0.20059\text{g}}{3.776 \text{ g sample}} \times 100\% = 6.472\%$$

Ex. 13-12 A 0.4755-g sample $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \text{ and inert }]/\text{H}_2\text{O}$, added KOH to alkaline $[\text{NH}_4^+ \rightarrow \text{NH}_3]$, distilled into 50.00 mL of 0.05035 M H_2SO_4 . Then back titration with 11.13 mL of 0.1214 M NaOH. Calculate (a) the % N (14.007 g/mol) and (b) the % $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (124.10 g/mol) in the sample.

$$\begin{aligned} \text{(a) \% N} &= \frac{(50.00 \times 0.05035 \times 2 - 11.13 \times 0.1214) \times 14.007}{0.4755 \text{ g} \times 1000} \times 100\% \\ &= \frac{3.6838 \times 14.007}{475.5} \times 100\% = 10.85\% \end{aligned}$$

$$\begin{aligned} \text{(b) \% } (\text{NH}_4)_2\text{C}_2\text{O}_4 &= \frac{3.6838 \times 124.10 / 2}{0.4755 \text{ g} \times 1000} \times 100\% = \frac{228.58}{475.5} \times 100\% \\ &= 48.07\% \end{aligned}$$

13D Gravimetric Titrimetry

13 E Titration curves in Titrimetric Methods

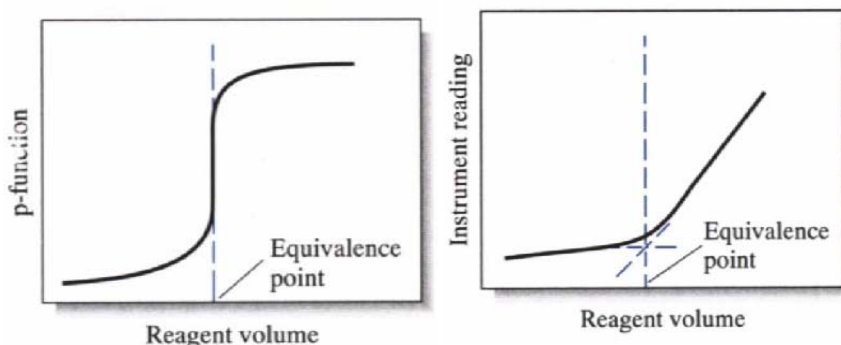


Fig. 13-2
Two types of
titration curves.

(a) Sigmoidal curve

(b) Linear-segment curve

Table 13-1 Concentration changes during a titration of 50.00 mL of 0.1000M AgNO_3 with 0.1000M KSCN

0.1000M KSCN, mL	$[\text{Ag}^+]$ mmol/L	mL of KSCN to cause a tenfold decrease in $[\text{Ag}^+]$	pAg	pSCN
0.00	1.000×10^{-1}		1.00	
40.91	1.000×10^{-2}	40.91	2.00	10.00
49.01	1.000×10^{-3}	8.10	3.00	9.00
49.90	1.000×10^{-4}	0.89	4.00	8.00
49.99	1.000×10^{-5}	0.09	5.00	7.00
50.00	1.000×10^{-6}	0.01	6.00	6.00
50.01	1.000×10^{-7}	0.01	7.00	5.00
50.10	1.000×10^{-8}	0.09	8.00	4.00
51.01	1.000×10^{-9}	0.91	9.00	3.00
61.11	1.000×10^{-10}	10.10	10.00	2.00

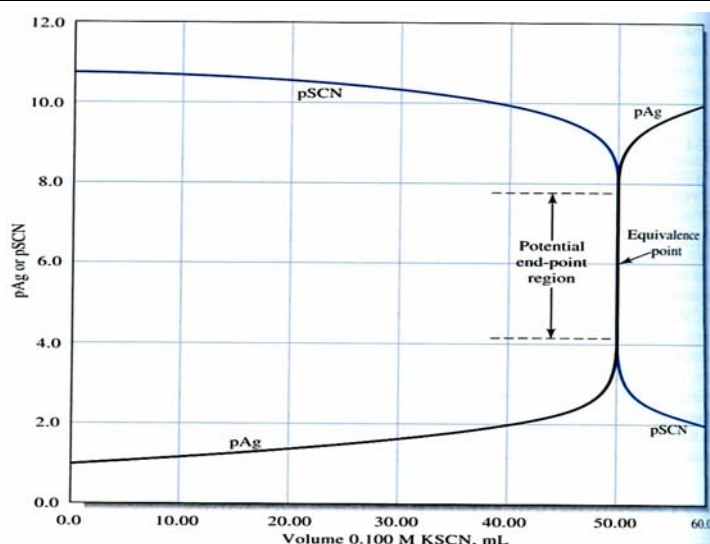


Fig. 13-3 Titration curve for the titration of 50.00 mL of 0.1000 M AgNO₃ with 0.1000 M KSCN.

13F Precipitation Titrimetry

Silver nitrate titrations : Argentometric methods

for : halides, halide-like anion (SCN⁻, CN⁻, CNO⁻) several divalent anions, mercaptans, fatty acids and several divalent and trivalent inorganic anions.

End point:

1. A change in color due to the reagent, the analyte or an indicator.
2. A change in potential of an electrode that responds to the conc. of one of the reactants.

Titration curves: plots of a conc.-related variable as a function of reagent volume.

13F-1 Precipitation titration curves involving silver ion

- ◆ preequivalence points
- ◆ equivalence point
- ◆ post equivalence points

Ex. 13-13. Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃.



◆ **Initial point:** 0.000 M in Ag, and pAg is indeterminate.

◆ preequivalence points , **At 10.00 mL**

$$\begin{aligned} [\text{Cl}^-] &\approx C_{\text{NaCl}} = \frac{\text{original no. mmol Cl}^- - \text{no. mol AgNO}_3}{\text{total volume of solution}} \\ &= \frac{50.00 \times 0.0500 - 10.00 \times 0.100}{50.00 + 10.0} = 0.02500 \text{ M} \end{aligned}$$

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{0.02500} = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}, \quad \text{pAg} = -\log(7.28 \times 10^{-9}) = \underline{\underline{8.14}}$$

◆ **Equivalence point**

$$[\text{Ag}^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}, \quad \text{pAg} = -\log(1.35 \times 10^{-5}) = \underline{4.87}$$

◆ **post equivalence point, After Addition of 26.0 mL of Reagent**

$$[\text{Ag}^+] \approx C_{\text{AgNO}_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.0500)}{76.00} = 1.316 \times 10^{-3}$$

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

Tab.13-2 Changes in pAg in the titration of Cl⁻ with AgNO₃.

AgNO ₃ , mL	50.00 mL of 0.0500 M NaCl with 0.1000M AgNO ₃	50.00 mL of 0.00500 M NaCl with 0.01000M AgNO ₃
10.00	8.04	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

The shapes of titration curves

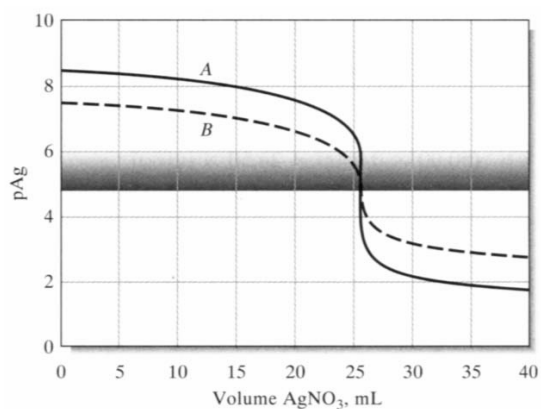


Fig. 13-4 Titration curve for A, 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃, and B, 50.00 mL of 0.00500 M NaCl with 0.01000 M AgNO₃.

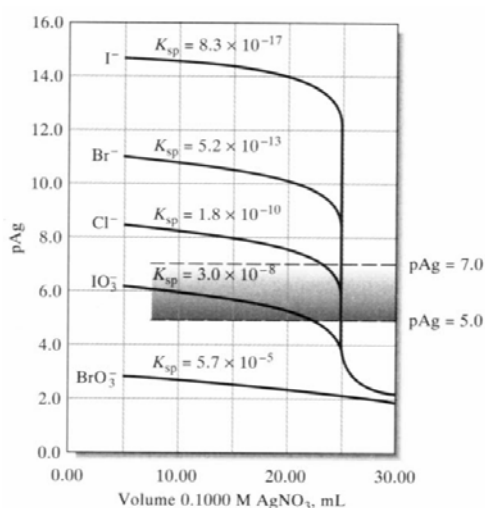


Fig. 13-5 Effect of reaction completeness on precipitation titration curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M AgNO₃.

***Factors influencing end-point sharpness**

Satisfactory end points require a change of 2 in p-function within ±0.1 mL of the equivalence point

- a. reagent conc. : conc. $\uparrow \rightarrow$ sharpness \uparrow
 b. reaction completeness : product ppt $K_{sp} \downarrow \rightarrow$ sharpness \uparrow

*Chemical indicators for precipitation titration



For a color change to be seen, $[InR]/[In]$ must change by a factor of 10 to 100.

13F-2 Titration curves for mixtures of anions

Titration of 50.00 mL of a solution ($[I^-] = 0.0500M$ and $[Cl^-]=0.0800 M$) with $0.1000 M AgNO_3$.

$$\frac{[Ag^+][I^-]}{[Ag^+][Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7} \Rightarrow [I^-] = (4.56 \times 10^{-7})[Cl^-]$$

after added 25.00 mL $AgNO_3$,

$$c_{Cl} = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533 M, \quad [I^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8} M$$

$$\text{no. mmol } I^- = 75.00 \text{ mL} \times (2.43 \times 10^{-8} \text{ mmol } I^-/\text{mL}) = 1.82 \times 10^{-6}$$

$$I^- \text{ unprecipitated} = \frac{1.82 \times 10^{-6}}{50.00 \times 0.0500} \times 100\% = 7.3 \times 10^{-5} \%$$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9} \Rightarrow pAg = -\log(3.41 \times 10^{-9}) = 8.47$$

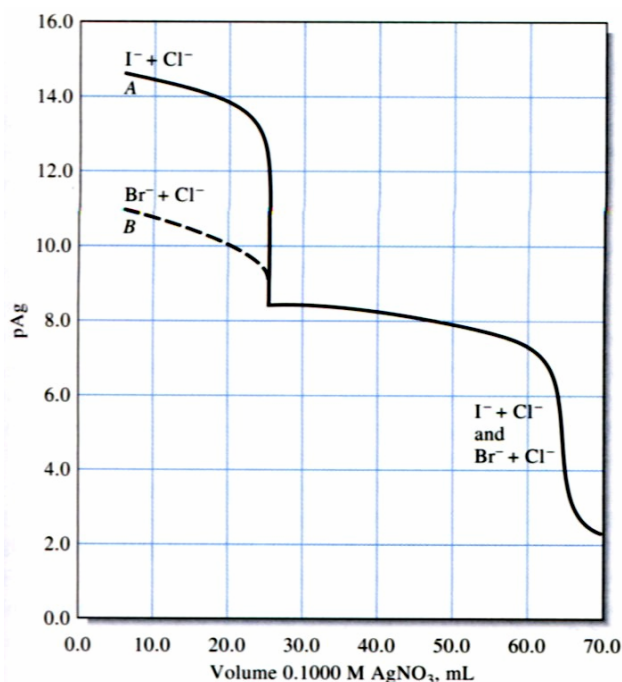
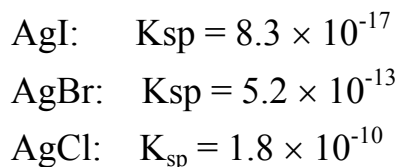
after added 30.00 mL $AgNO_3$,

$$c_{Cl} = [Cl^-] = \frac{50.00 \times 0.0800 - (30.00 \times 0.100 - 50.00 \times 0.0500)}{50.00 + 30.00} = 0.0438 M$$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9},$$

$$pAg = 8.38$$

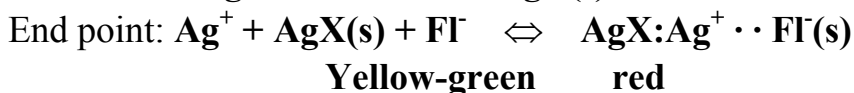
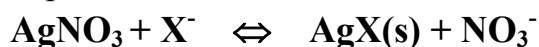
Fig. 13-6 Titration curves for 50.00 mL of a solution 0.0800 M in Cl^- and 0.0500 M in I^- or Br^- .



2. Adsorption indicators: The Fajans method

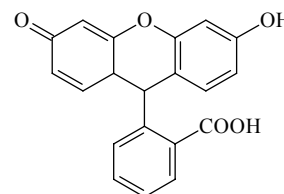
1926, Polish chemist, K. Fajans

Advantages: rapid, accurate and reliable



Indicator: Fluorescein anion

- * avoid ppt coagulation → ppt surface ↑
 - a. adding dextrin or polyethylene glycol
 - b. quick titration and avoid excessive stirring
 - c. halide ion conc. : 0.005 ~ 0.025 M



fluorescein

*Fluorescein dyes: weak ionized acids

pH ↓ → [Fl⁻] ↓ → weak end point

pH ≥ 7, (dichlorofluorescein: pH ≥ 4)

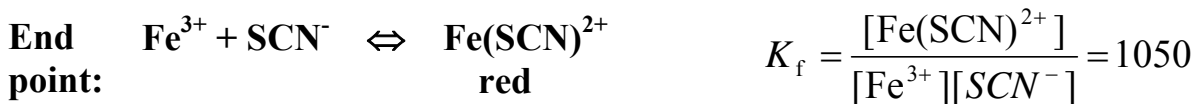
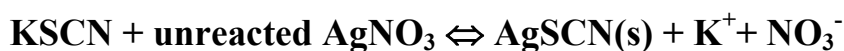
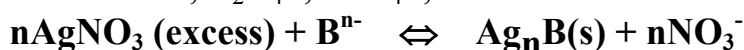
*Photochemical decomposition : ppt → black

Indicator	pH	Sample
Fluorescein	≥ 7	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻
Dichlorofluorescein	≥ 4	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻
Eosin	≥ 2	Br ⁻ , I ⁻ , SCN ⁻

3. Iron(III) Ion; The Volhard method

1874 Jacob Volhard, a German chemist, (back titration): Iron(III) ion as indicator

sample: halide ion, C₂O₄²⁻, AsO₄³⁻, SCN⁻



*pH : in acidic soln to prevent Fe(III) → Fe(OH)₃(s)

*advantage: carbonate, oxalate & arsenate do not interfere.

*For Cl⁻ ion in blood serum, urine. (sample: HNO₃ digestion)

*Quantitativeness of the back titration



a. compare AgSCN and Ag_nB : molar solubility AgSCN: 1.0 × 10⁻⁶ M

b. Calculate K_{rxn}
$$K_{\text{rxn}} = \frac{[\text{B}^{n-}]}{[\text{SCN}^-]^n} = \frac{K_{\text{sp}} \text{ of Ag}_n\text{B}}{(K_{\text{sp}} \text{ of AgSCN})^n}$$

if AgSCN solubility < Ag_nB or K_{rxn} > 1

→ **filter Ag_nB ppt or adding liquid nitrobenzene**

Table 13-3 Typical Argentometric Precipitation Methods

Analyte	End point	Remarks
AsO ₄ ³⁻ , Br ⁻ , I ⁻ , CNO ⁻ , SCN ⁻	Volhard	Removal of Ag salt not required
CO ₃ ²⁻ , CrO ₄ ²⁻ , CN ⁻ , Cl ⁻ , C ₂ O ₄ ²⁻ , PO ₄ ³⁻ , S ²⁻ , NCN ²⁻	Volhard	Removal of Ag salt required before back-titration of excess Ag ⁺
BH ₄ ⁻	Modified Volhard	Titration of excess Ag ⁺ following BH ₄ ⁻ + 8Ag ⁺ + 8OH ⁻ → 8Ag(s) + H ₂ BO ₃ ⁻ + 5H ₂ O
Epoxide	Volhard	Titration of excess Cl ⁻ following hydrohalogenation
K ⁺	Modified Volhard	Precipitation of K ⁺ with known excess of B(C ₆ H ₅) ₄ ⁻ , addition of excess Ag ⁺ giving AgB(C ₆ H ₅) ₄ (s), and back-titration of the excess
Br ⁻ , Cl ⁻	Mohr method	In neutral solution
Br ⁻ , Cl ⁻ , I ⁻ , SeO ₃ ²⁻	Adsorption indicator	
V(OH) ₄ ⁺ , fatty acids, mercaptans	Electroanalytical	Direct titration with Ag ⁺
Zn ²⁺	Modified Volhard	Precipitation as ZnHg(SCN) ₄ , filtration, dissolution in acid, addition of excess Ag ⁺ , back-titration of excess Ag ⁺
F ⁻	Modified Volhard	Precipitation as PbClF, filtration, dissolution in acid, addition of excess Ag ⁺ , back-titration of excess Ag ⁺

Ex. The As in a 9.13-g sample of pesticide was converted to AsO₄³⁻ and precipitated as Ag₃AsO₄ with 50.00 mL of 0.02015 M AgNO₃. The excess Ag⁺ was then titrated with 4.75 mL of 0.04321 M KSCN. Calculate the % of As₂O₃ in the sample.

no. mmol AgNO₃ = 50.00 mL × 0.02015 mmol = 1.0075

no. mmol KSCN = 4.75 mL × 0.04321 mmol = 0.2052

no. mmol AgNO₃ consumed by AsO₄³⁻ = 0.8023

As₂O₃ ≡ 2 AsO₄³⁻ ≡ 6 AgNO₃

% As₂O₃ = 0.8023 × (1/6) × 0.1978/9.13 × 100 % = 0.2987 %

*Quantitativeness of AgNO₃ titration



a. **99.9 % reaction:** at equivalence point, max % Cl⁻ : 0.1 %

ex: AgCl, $K_{\text{sp}} = 1.8 \times 10^{-10}$; $[\text{Cl}^-] = \sqrt{K_{\text{sp}}} = 1.34 \times 10^{-5} \text{ M}$

$$\% \text{dissolved} = \frac{\sqrt{K_{\text{sp}} \text{ of AgCl}} \times 100}{\text{M of initial Cl}^-} = \frac{1.34 \times 10^{-5} \times 100}{0.010 \text{ M}} = 0.13\%$$

b. min. theo. $K_{\text{rxn}} \leftrightarrow K_{\text{rxn}}$

$$K_{\text{rxn}} = 1/K_{\text{sp}}$$

0.10 M sample $[\text{X}^-] \rightarrow 0.1 \%$

upper limit of $[\text{X}^-] = (0.10 \text{ M})(0.1 \%) = 10^{-4} \text{ M}$

equivalence point : $[\text{Ag}^+] = [\text{X}^-]$

$$\text{min theo. } K_{\text{rxn}} = \frac{1}{(10^{-4} \text{ M Ag}^+)(10^{-4} \text{ M X}^-)} = 10^8$$

for 0.1 M X⁻, actual $K_{\text{rxn}} \geq 10^8$

for 0.01 M X⁻, actual $K_{\text{rxn}} \geq 10^{10}$