Principles of Volumetric Analysis

- titration
  - titrant
  - analyte
  - indicator
  - equivalence point vs. end point
  - titration error
  - blank titration

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Principles of Volumetric Analysis

primary standard

1. High purity 100.02%
2. Stability toward air
3. Absence of hydrate water
4. Available at moderate cost
5. Soluble

Principles of Volumetric Analysis

standardization

- standard solution

Methods for establishing concentration

- direct method
- standardization
- secondary standard solution

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Volumetric Procedures and Calculations

relate the moles of titrant to the moles of analyte

moles titrant = # moles analyte

$$\#moles_{titrant} = (V*M)_{titrant}$$

$$=$$

$$\#moles_{analyte} = (V*M)_{analyte}$$

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EXAMPLE: What is the molarity of an HCl solution if it took 39.72 mL of the 0,09782 M NaOH solution to titrate 25.00 mL HCl solution?

EXAMPLE: What is the molarity of an HCl solution if it took 39.72 mL of the above NaOH solution to titrate 25.00 mL HCl solution?

at equivalence point:

$$\# \text{ moles}_{acid} = \# \text{ moles}_{bases}$$

$$V_{acid} \times M_{acid} = V_{base} \times M_{base}$$

EXAMPLE: What is the molarity of an HCl solution if it took 39.72 mL of the above NaOH solution to titrate 25.00 mL HCl solution?

at equivalence point:

$$\# \, mL_{acid} \times M_{acid} = \# \, mL_{base} \times M_{base}$$

$$M_{acid} = \frac{\# \, mL_{base} \times M_{base}}{\# \, mL_{acid}}$$

EXAMPLE: What is the molarity of an HCl solution if it took 39.72 mL of the above NaOH solution to titrate 25.00 mL HCl solution?

at equivalence point:

$$M_{acid} = \frac{\#\ mL_{base} \times M_{base}}{\#\ mL_{acid}}$$

$$= \frac{(39.72\ mL)(0.09782\ M)}{(25.00\ mL)} = 0.1554\ M$$

Acid-Base Indicators

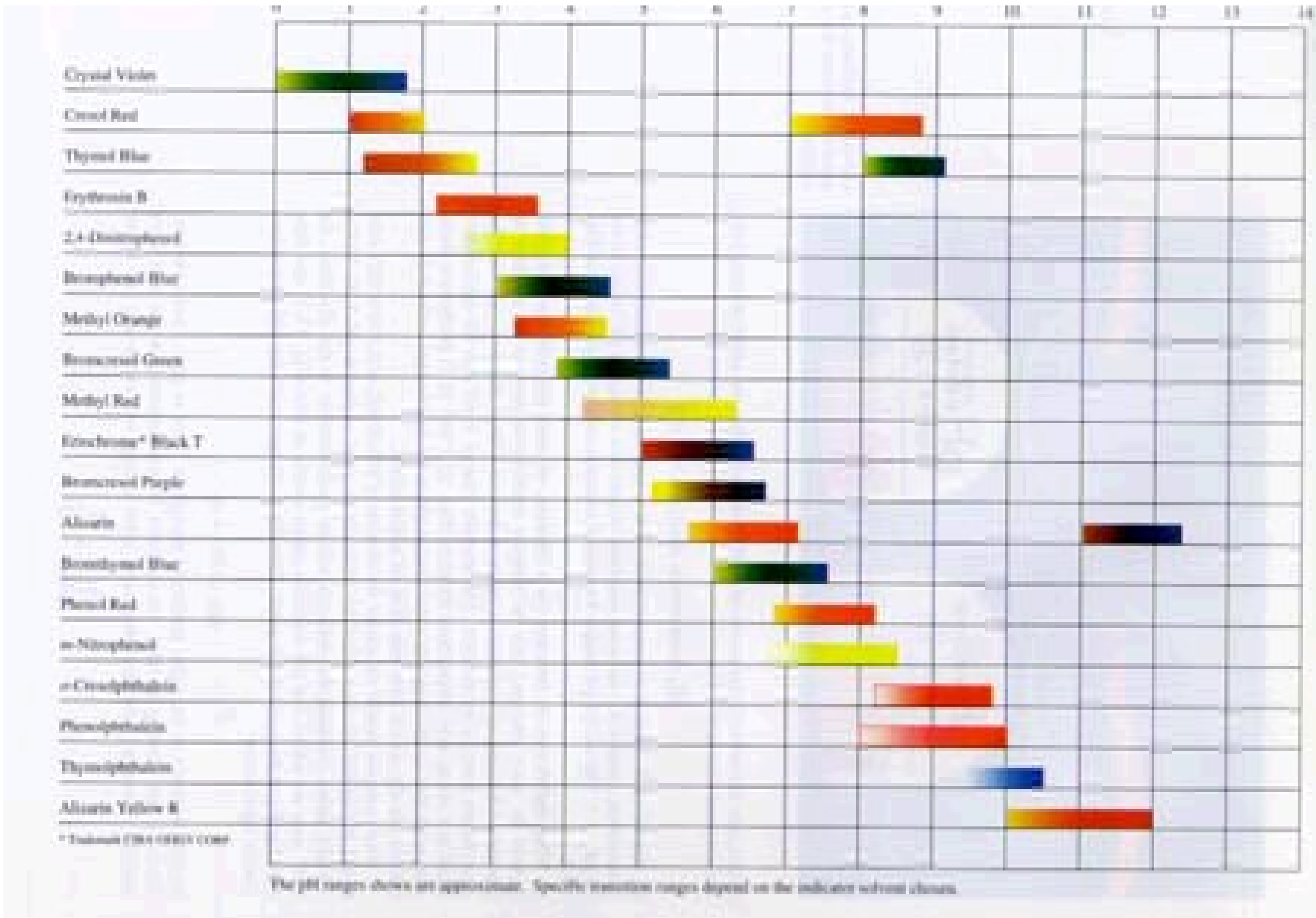

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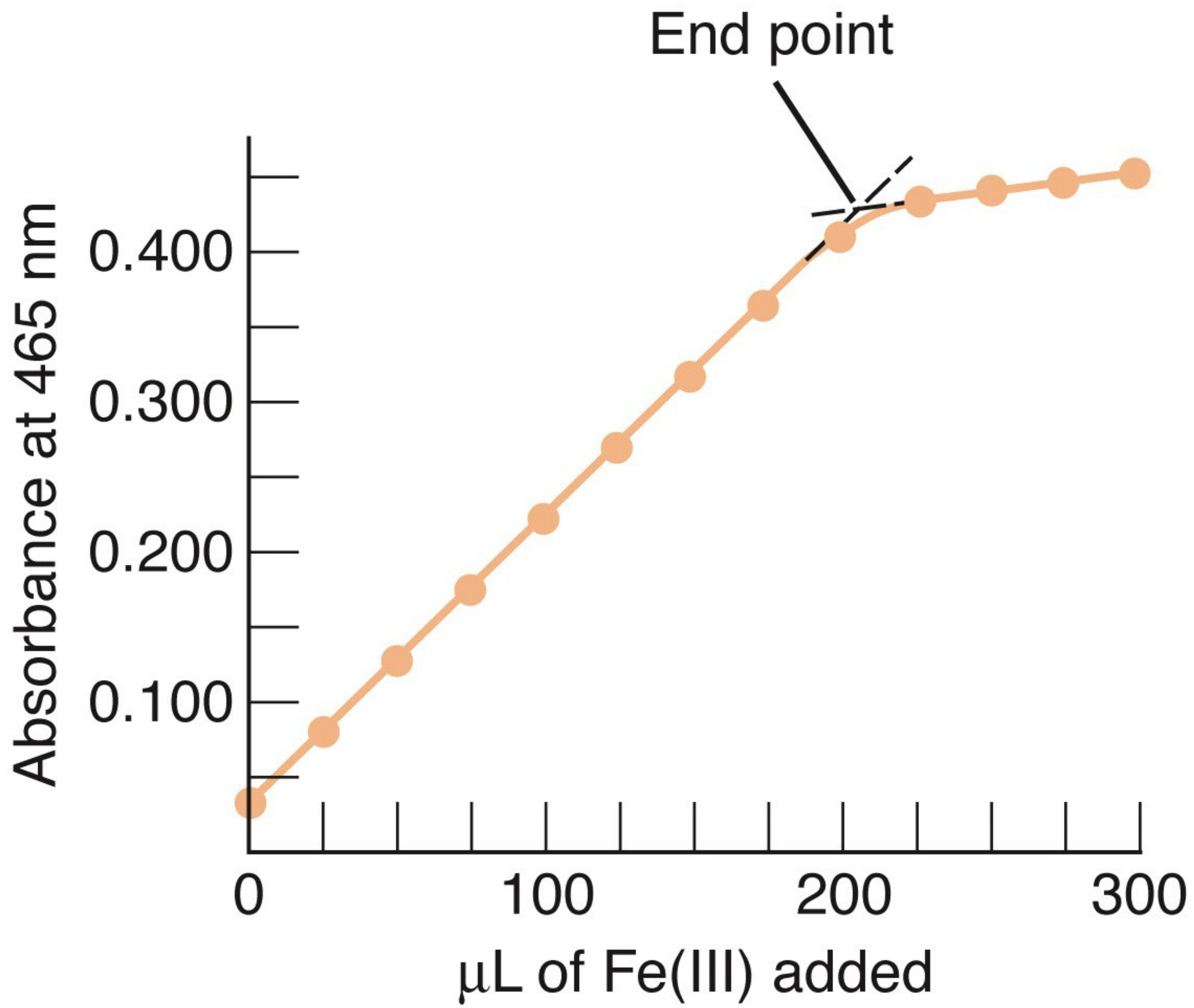
Figure 7.5 Spectrophotometric Titration



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Precipitation Titration Curve

p-function $pX = -\log_{10}[X]$

precipitation titration curve

- four types of calculations
  - initial point
  - before equivalence point
  - equivalence point
  - after equivalence point

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Precipitation Titration Curve

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

titration curve => pAg vs. vol. $AgNO_3$ added

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

titration curve => pAg vs. vol. $AgNO_3$ added

initial point

after 0.0 mL of $AgNO_3$ added

at the initial point of a titration of any type, only analyte is present, no titrant is present, therefore pAg can not be calculated.

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

pAg can be accurately calculated only after some AgBr has started to form. This may take a few mL of titrant

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$M_{NaBr\ unreacted} = \frac{V_{NaBr} * M_{NaBr} - V_{AgNO3} * M_{AgNO3}}{V_{NaBr} + V_{AgNO3}}$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$M_{NaBr\ unreacted} = \frac{V_{NaBr} * M_{NaBr} - V_{AgNO3} * M_{AgNO3}}{V_{NaBr} + V_{AgNO3}}$$

$$M_{NaBr\ unreacted} = \frac{(50.00\text{mL}*0.00500\text{M}) - (5.00\text{mL}*0.01000\text{M})}{(50.00 + 5.00)\text{mL}}$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$M_{NaBr\ unreacted} = \frac{(50.00mL*0.00500M) -(5.00mL*0.01000M)}{(50.00 + 5.00)mL}$$

$$M_{NaBr\ unreacted} = 3.64 \times 10^{-3} M$$

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EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$M_{NaBr\ unreacted} = 3.64 \times 10^{-3} M$

$[Br^-]_{total} = [Br^-]_{NaBr\ unreacted} + [Br^-]_{dissolved\ AgBr}$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$M_{NaBr\ unreacted} = 3.64 \times 10^{-3} M$$

$$[Br^-]_{total} = [Br^-]_{NaBr\ unreacted} + [Br^-]_{dissolved\ AgBr}$$

$$[Br^-]_{total} = 3.64 \times 10^{-3} M + [Ag^+]_{dissolved\ AgBr}$$

where $[Br^-]_{dissolved\ AgBr} = [Ag^+]_{dissolved\ AgBr}$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$[Br^-]_{total} = 3.64 \times 10^{-3} M + [Ag^+]_{dissolved\ AgBr}$$

where $[Br^-]_{dissolved\ AgBr} = [Ag^+]_{dissolved\ AgBr}$

except very near the equivalence point,

$$3.64 \times 10^{-3} M >> [Ag^+]_{dissolved\ AgBr}$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$[Br^-]_{total} = 3.64 \text{ X } 10^{-3}M + [Ag^+]_{dissolved\ AgBr}$$

except very near the equivalence point,

$$3.64 \text{ X } 10^{-3}M >> [Ag^+]_{dissolved\ AgBr}$$

thus $[Br^-]_{total} \sim 3.64 \text{ X } 10^{-3}M$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$[Br^-]_{total} \sim 3.64 \text{ X } 10^{-3} M$$

$$pBr = - \log_{10}(3.64 \text{ X } 10^{-3}) = 2.44$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$K_{sp} = [Ag^+][Br^-] = 5.2 \text{ X } 10^{-13} M^2$$

$$- \log K_{sp} = - \log[Ag^+] - \log[Br^-]$$

$$= - \log(5.2 \text{ X } 10^{-13})$$

$$pK_{sp} = pAg + pBr = 12.28$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

before equivalence point

after 5.0 mL of $AgNO_3$ added

$$K_{sp} = [Ag^+][Br^-] = 5.2 \text{ X } 10^{-13} M^2$$

$$-\log K_{sp} = -\log[Ag^+] - \log[Br^-]$$

$$= -\log(5.2 \text{ X } 10^{-13})$$

$$pK_{sp} = pAg + pBr = 12.28$$

if pBr = 2.44

$$pAg = pK_{sp} - pBr = 12.28 - 2.44 = 9.84$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

equivalence point

at 25.00 mL of $AgNO_3$ added

At the equivalence point, $[Ag^+] = [Br^-]$

thus

$$K_{sp} = [Ag^+][Br^-] = 5.2 \text{ X } 10^{-13} M^2$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

equivalence point

at 25.00 mL of $AgNO_3$ added

becomes when $[Ag^+] = [Br^-]$

$$[Ag^+]^2 = 5.2 \times 10^{-13} M^2$$

$$[Ag^+] = 7.21 \times 10^{-7} M$$

$$pAg = 6.14$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

after equivalence point

After the equivalence point there is very little change in the amount of precipitate present (except very close to the equivalence point)

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

after equivalence point

thus, at 25.10 mL of $AgNO_3$ added

$$M_{AgNO3\ unreacted} = \frac{V_{AgNO3} * M_{AgNO3} - V_{NaBr} * M_{NaBr}}{V_{AgNO3} + V_{NaBr}}$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

after equivalence point

thus, at 25.10 mL of $AgNO_3$ added

$$M_{AgNO3\ unreacted} = \frac{V_{AgNO3} * M_{AgNO3} - V_{NaBr} * M_{NaBr}}{V_{AgNO3} + V_{NaBr}}$$

$$M_{AgNO3\ unreacted} = \frac{(25.10\ mL * 0.01000\ M) - (50.00\ mL * 0.00500\ M)}{(25.10 + 50.00) mL}$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

after equivalence point

thus, at 25.10 mL of $AgNO_3$ added

$$M_{AgNO3\ unreacted} = \frac{(25.10\ mL * 0.01000\ M) - (50.00\ mL * 0.00500\ M)}{(25.10 + 50.00)mL}$$

$$M_{AgNO3\ unreacted} = 1.33 \times 10^{-5} M$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

after equivalence point

thus, at 25.10 mL of $AgNO_3$ added

$$M_{AgNO3\ unreacted} = 1.33 \times 10^{-5} M$$

$$[Ag^+]_{total} = [Ag^+]_{AgNO3\ unreacted} + [Ag^+]_{dissolved\ AgBr}$$

EXAMPLE: Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$.

after equivalence point

thus, at 25.10 mL of $AgNO_3$ added

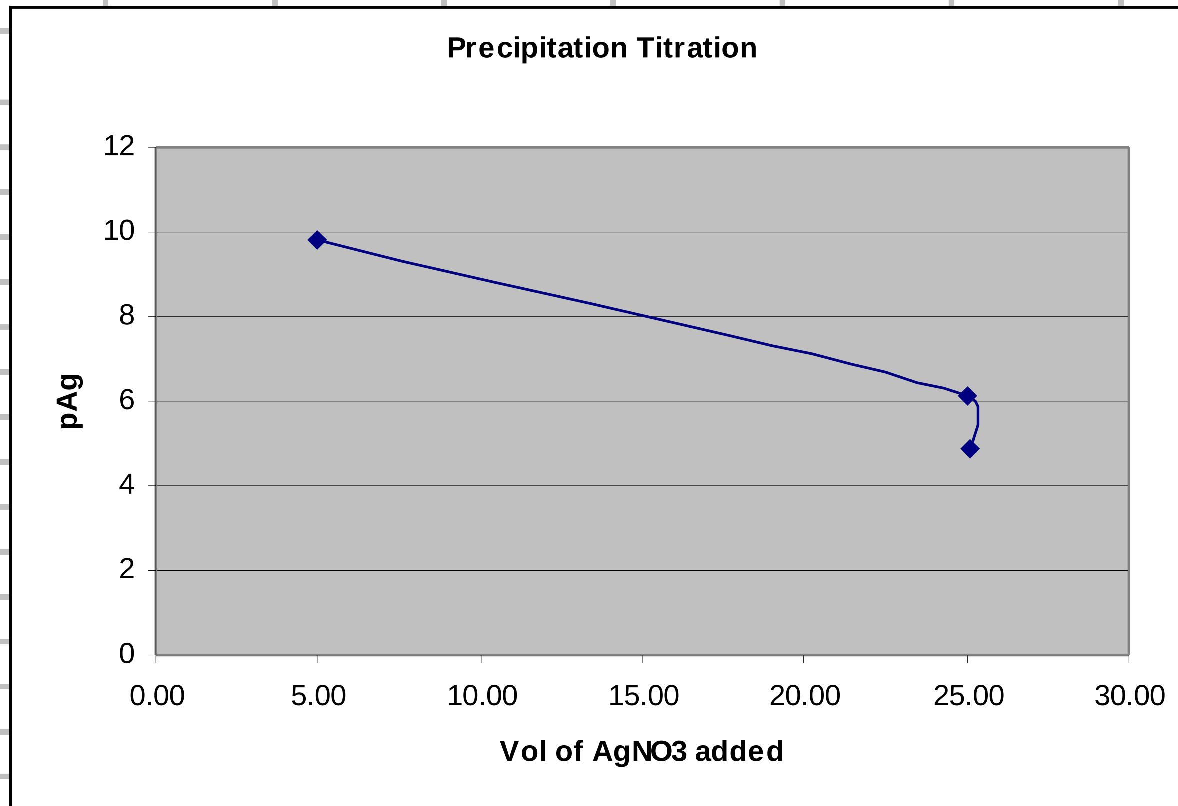
$$[Ag^+]_{total} = [Ag^+]_{AgNO3\ unreacted} + [Ag^+]_{dissolved\ AgBr}$$

0

$$[Ag^+]_{total} = 1.33 \text{ X } 10^{-5}M + [Ag^+]_{dissolved\ AgBr}$$

$$[Ag^+]_{total} \sim 1.33 \text{ X } 10^{-5}M$$

Vol of	pAg
5.00	9.84
25.00	6.14
25.10	4.88



Vol of t	pAg		
5.00	9.84		
10.00	9.68	2.60	0.0025
15.00	9.47	2.81	0.001538
20.00	9.13	3.15	0.000714
21.00	9.03	3.25	0.000563
22.00	8.90	3.38	0.000417
23.00	8.72	3.56	0.000274
24.00	8.41	3.87	0.000135
24.50	8.11	4.17	6.71E-05
25.00	6.14		
25.10	4.88		
26.00	3.88	0.0001316	
27.00	3.59	0.0002597	
28.00	3.41	0.0003846	
29.00	3.30	0.0005063	
30.00	3.20	0.000625	
35.00	2.93	0.0011765	
40.00	2.78	0.0016667	
45.00	2.68	0.0021053	

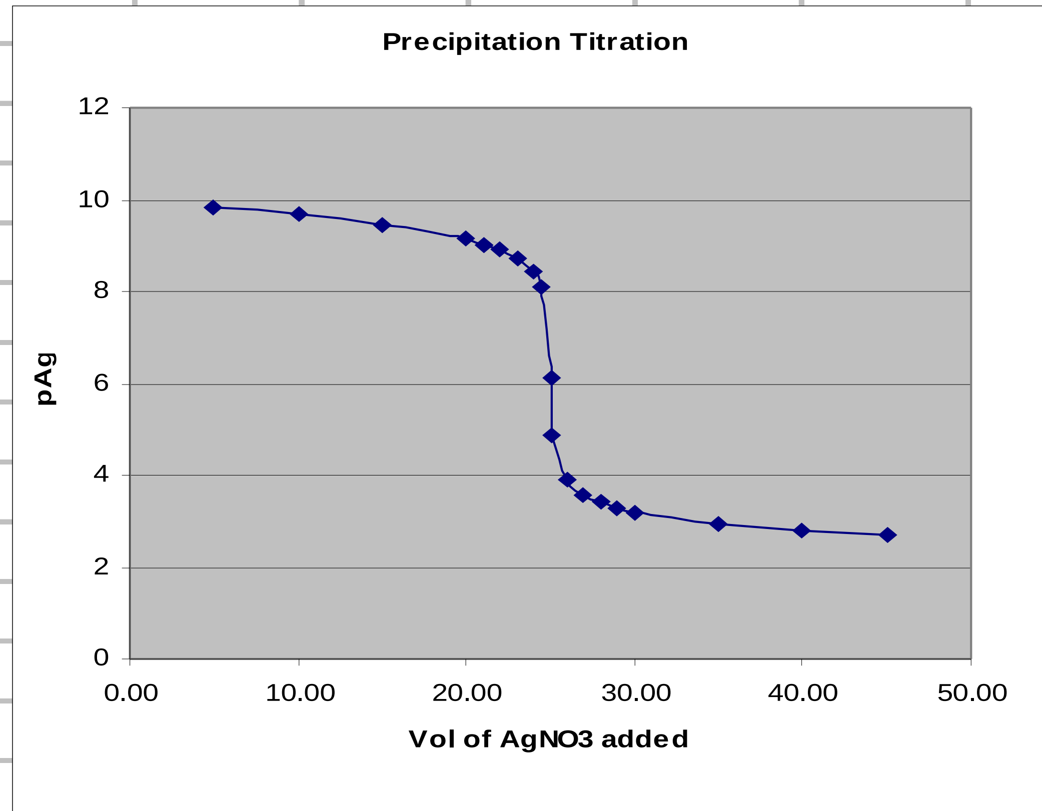
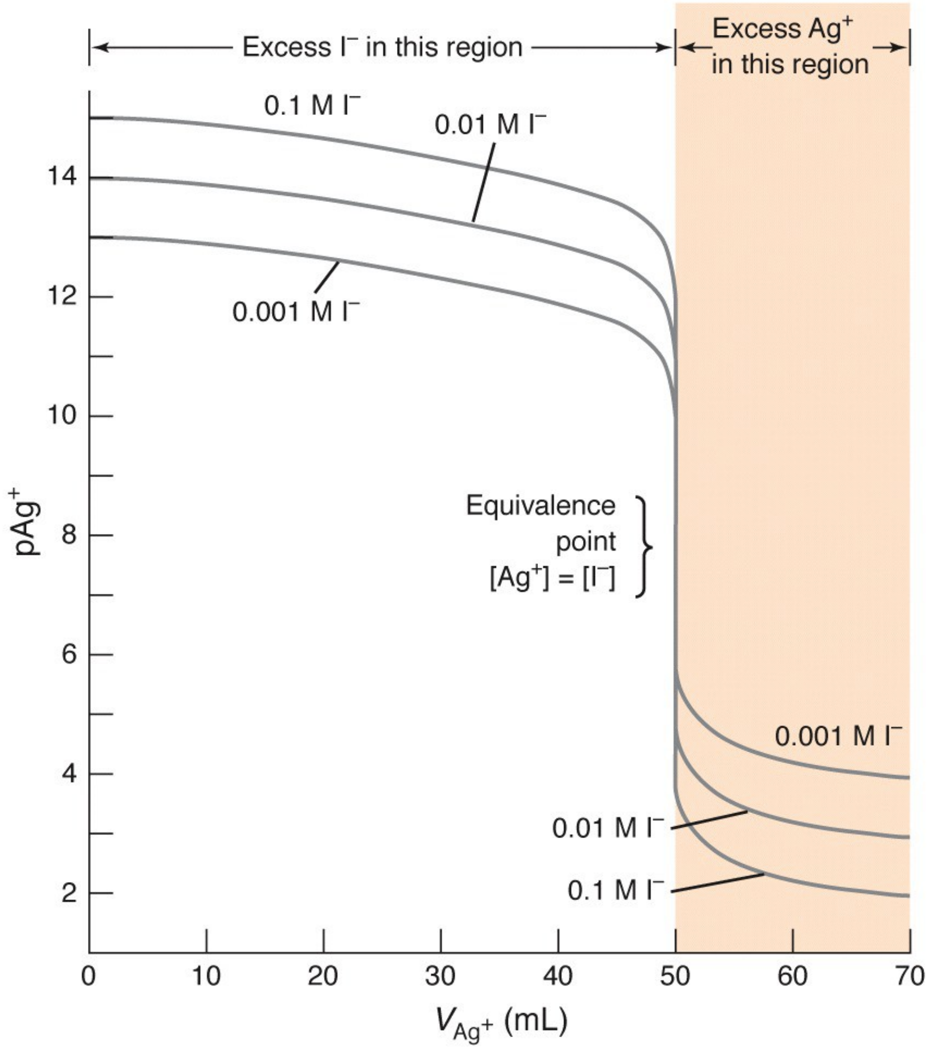


Figure 7.6 Precipitation titration Curves



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End-Point Detection

argentometric titrations

1. Mohr - titration of Cl^- with $AgNO_3$

   - K_2CrO_4 gives brick red color to precipitate, Ag_2CrO_4

End-Point Detection

argentometric titrations

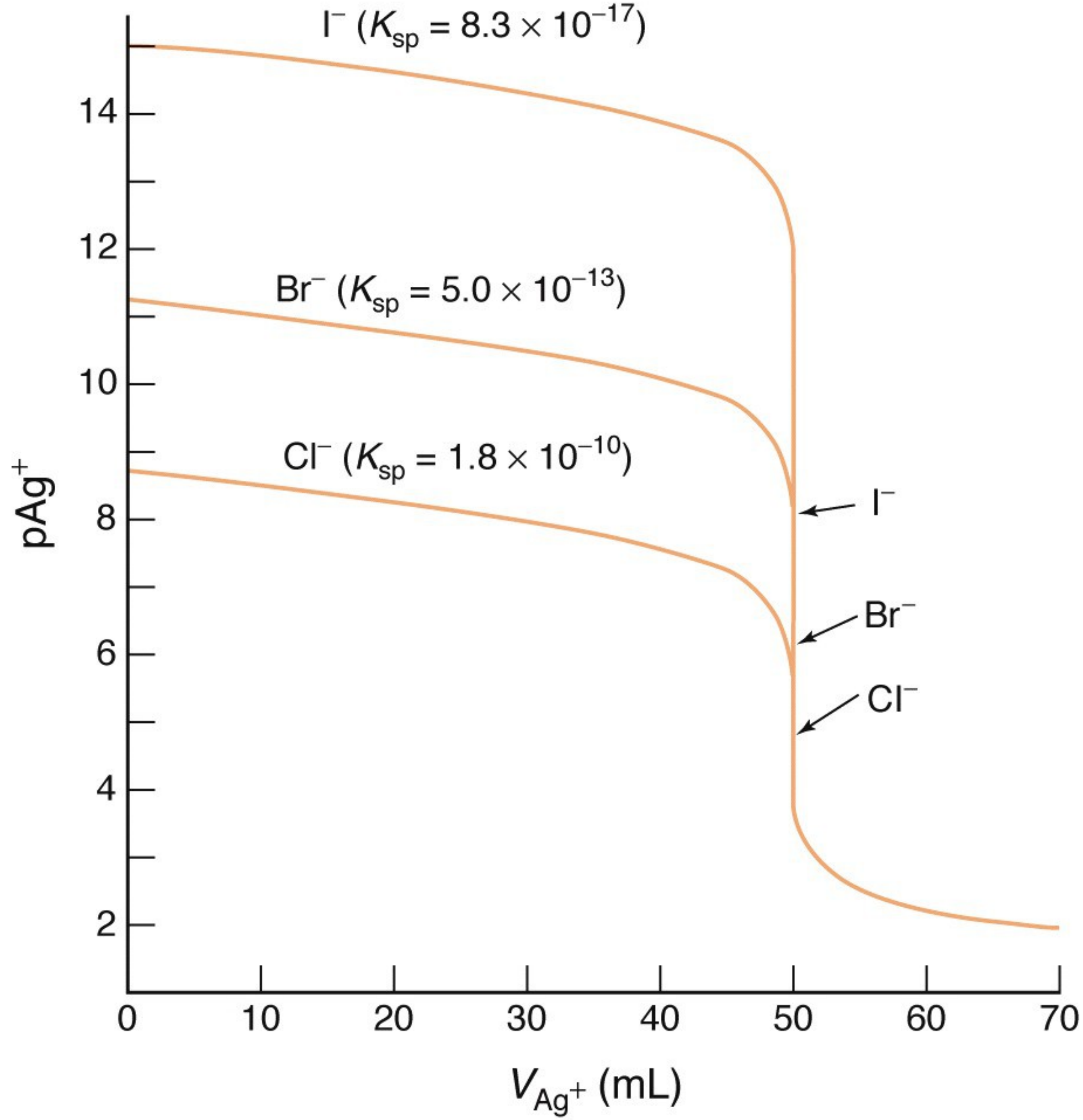
2. Volhard - titration of Ag^{+} with Cl^{-}
   - KSCN in the presence of Fe^{+3} gives blood red color to precipitate, $FeSCN^{+2}$

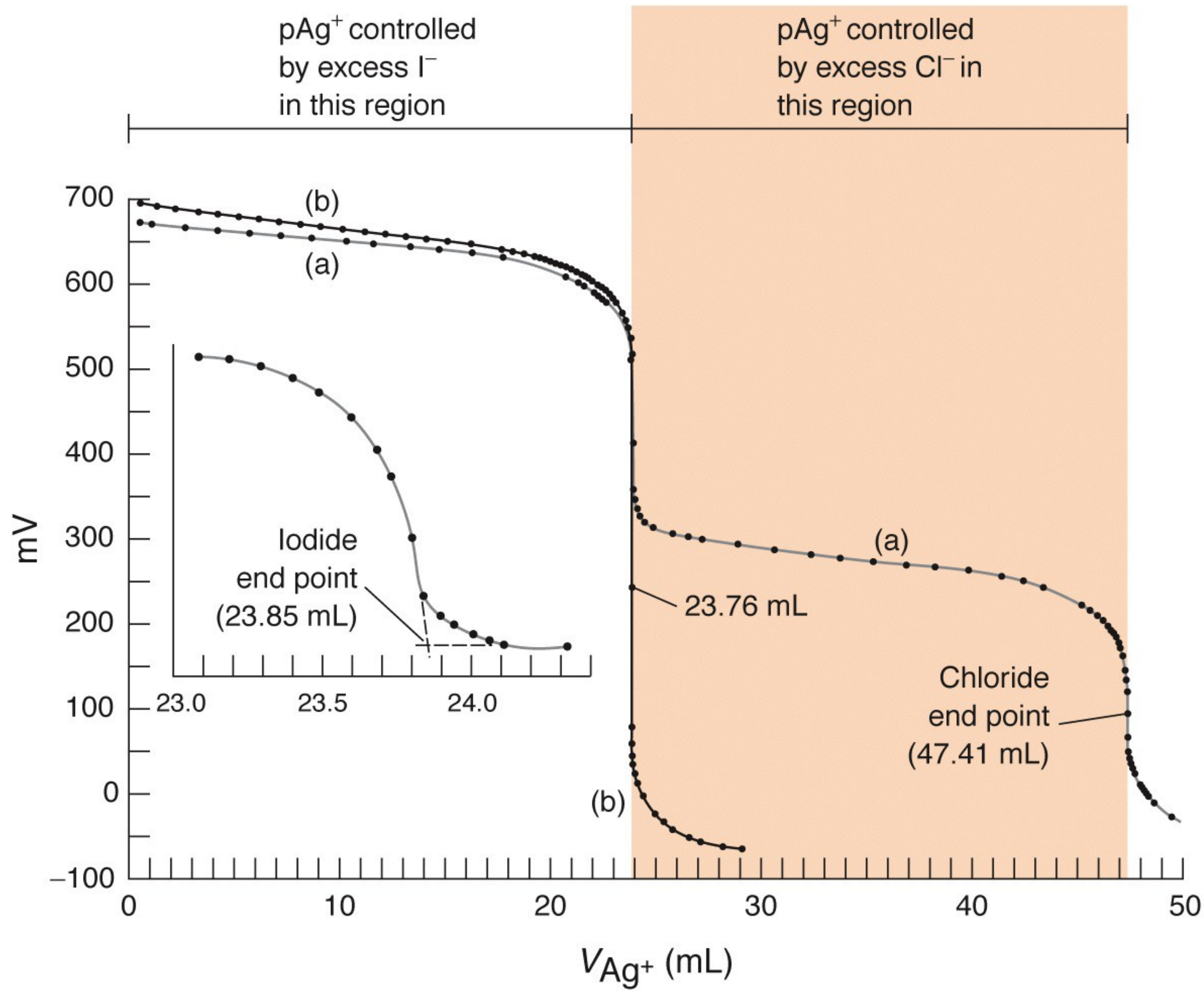
End-Point Detection

argentometric titrations

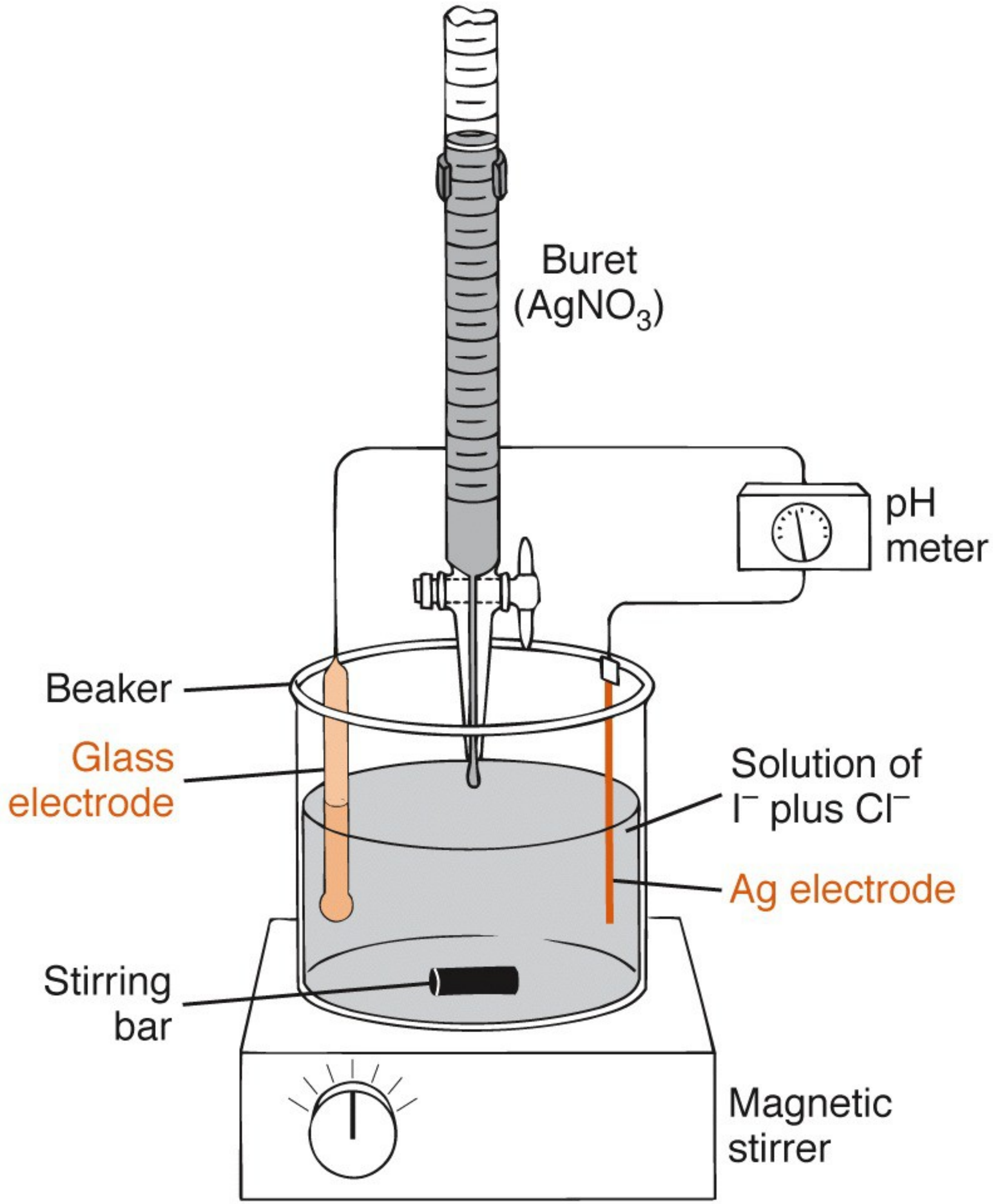
3. Fajans - titration of Cl^- with $AgNO_3$

- absorption indicator, dye absorbs on to the surface of the particles of AgCl, attracted by excess Cl^- absorbed on the surface of the precipitate


I^- ($K_{sp} = 8.3 \times 10^{-17}$)
Br^- ($K_{sp} = 5.0 \times 10^{-13}$)
Cl^- ($K_{sp} = 1.8 \times 10^{-10}$)
I^-
Br^-
Cl^-
pAg^+
14
12
10
8
6
4
2
0
10
20
30
40
50
60
70
V_{Ag^+} (mL)



pAg$^+$ controlled by excess I^- in this region
pAg$^+$ controlled by excess Cl^- in this region
700
600
500
400
300
200
100
0
−100
mV
(b)
(a)
Iodide end point (23.85 mL)
23.0
23.5
24.0
23.76 mL
(a)
Chloride end point (47.41 mL)
(b)
0
10
20
30
40
50
V_{Ag^+} (mL)


Buret
(AgNO3)
pH
meter
Beaker
Glass
electrode
Solution of
I⁻ plus Cl⁻
Ag electrode
Stirring
bar
Magnetic
stirrer

	A	B	C	D	E
1	Titration of I- with Ag+				
2					
3	Ksp(AgI) =	pAg	[Ag+]	[I-]	Vm
4	8.30E-17	15.08	8.32E-16	9.98E-02	0.035
5	Vo =	15	1.00E-15	8.30E-02	3.195
6	25	14	1.00E-14	8.30E-03	39.322
7	Co(I) =	12	1.00E-12	8.30E-05	49.876
8	0.1	10	1.00E-10	8.30E-07	49.999
9	Co(Ag) =	8	1.00E-08	8.30E-09	50.000
10	0.05	6	1.00E-06	8.30E-11	50.001
11		4	1.00E-04	8.30E-13	50.150
12		3	1.00E-03	8.30E-14	51.531
13		2	1.00E-02	8.30E-15	68.750
14	C4 = 10^-B4				
15	D4 = A4/C4				
16	E4 = A6*(A8+C4-D4)/(A10-C4+D4)				

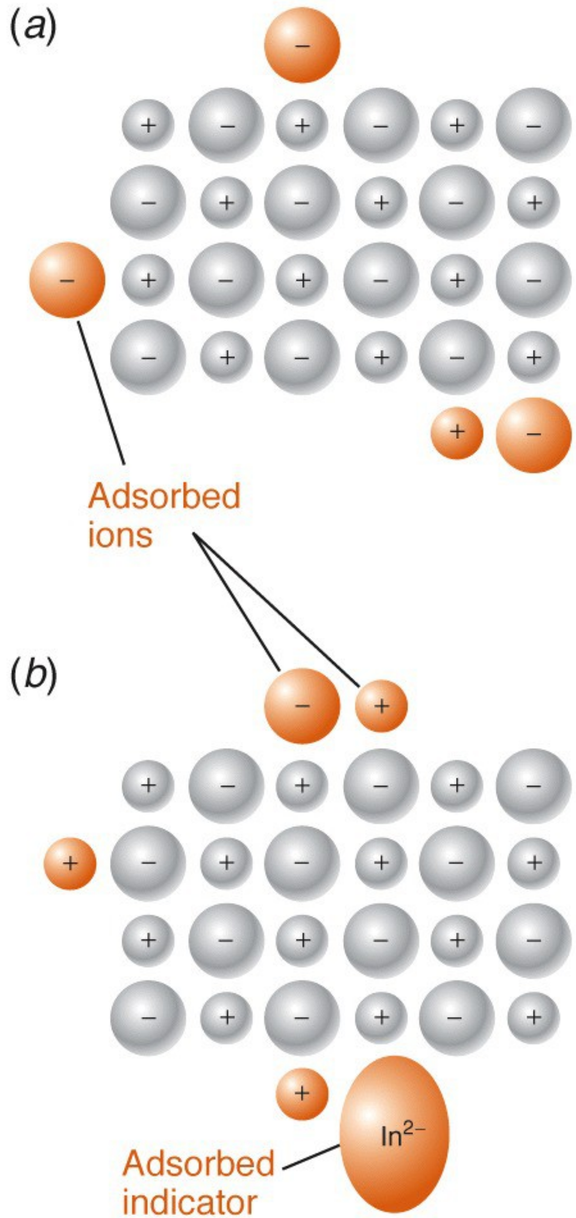

(a)
−
+
Adsorbed ions
(b)
In2−
Adsorbed indicator

Table 7-1 Applications of precipitation titrations

Species analyzed	Notes
	VOLHARD METHOD
Br^-, I^-, SCN^-, CNO^-, AsO_4^{3-}	Precipitate removal is unnecessary.
Cl^-, PO_4^{3-}, CN^-, $C_2O_4^{2-}$, CO_3^{2-}, S^{2-}, CrO_4^{2-}	Precipitate removal required.
BH_4^-	Back titration of Ag^+ left after reaction with BH_4^-: $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$
K^+	K^+ is first precipitated with a known excess of $(C_6H_5)_4B^-$. Remaining $(C_6H_5)_4B^-$ is precipitated with a known excess of Ag^+. Unreacted Ag^+ is then titrated with SCN^-.
	FAJANS METHOD
Cl^-, Br^-, I^-, SCN^-, $Fe(CN)_6^{4-}$	Titration with Ag^+. Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromophenol blue.
F^-	Titration with $Th(NO_3)_4$ to produce ThF_4. End point detected with alizarin red S.
Zn^{2+}	Titration with $K_4Fe(CN)_6$ to produce $K_2Zn_3[Fe(CN)_6]_2$. End-point detection with diphenylamine.
SO_4^{2-}	Titration with $Ba(OH)_2$ in 50 vol % aqueous methanol using alizarin red S as indicator.
Hg_2^{2+}	Titration with NaCl to produce Hg_2Cl_2. End point detected with bromophenol blue.
PO_4^{3-}, $C_2O_4^{2-}$	Titration with $Pb(CH_3CO_2)_2$ to give $Pb_3(PO_4)_2$ or PbC_2O_4. End point detected with dibromofluorescein (PO_4^{3-}) or fluorescein ($C_2O_4^{2-}$).