Precipitation Titration

Precipitation Titration of Br^-

- Titration reaction: $Br^-_{(aq)} + Ag^+_{(aq)} \Leftrightarrow AgBr_{(s)}$

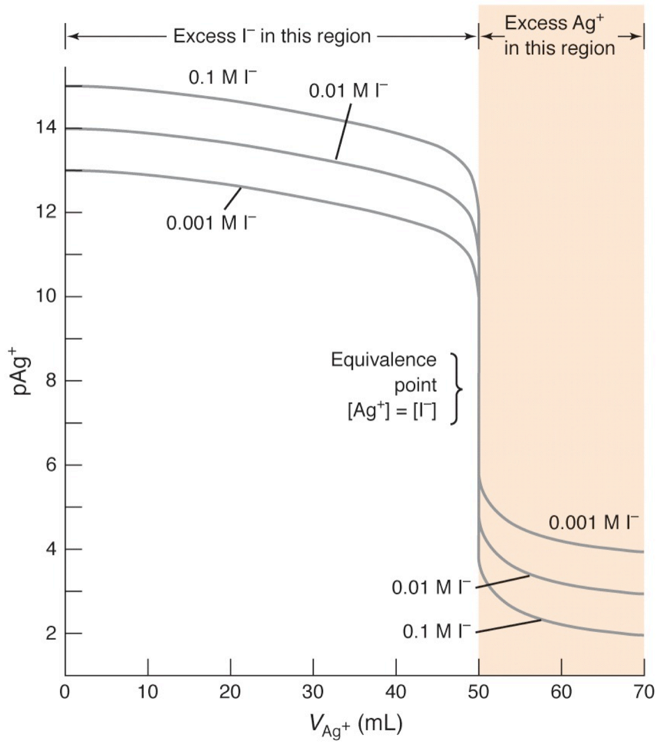
Titration Example: determine the titration curve.

> **We titrate 5.000 mL of 0.6000 M Br^-, to which we add 25.00 mL of deionized water, with 0.1000 M Ag^+ titrant.**
>
> Need to know:
> - moles of analyte (Br^-) initially present,
> - stoichiometry of the titration reaction,
> - then determine the volume required to reach the equivalence point.
>
> Moles Br^- = 0.005 000 L x 0.6000 mol/L = 3.000×10^{-3} mol
>
> Stoichiometry is 1:1
>
> $\therefore$ 3.000×10^{-3} mol Ag^+ need to reach equivalence point
>
> $V_{titrant}$ = (moles titrant needed) / (molarity titrant)
>
> $V_{Ag} = (3.000 \times 10^{-3}$ mol) / (0.1000 mol/L) = 0.030 00 L = 30.00 mL

- Knowing shape of titration curve enables selection an endpoint detection method, and understanding the performance of the titration.

- Express wide ranging concentration as pX

  pX = - log [x]



Four regions in titration curve**:**

1) **Initial** - analyte alone is present
2) **Before equivalence point** - analyte is in excess.
3) **Equivalence point** - amounts of unreacted analyte and titrant are very small
4) **Past equivalence point** - titrant is in excess

Region 1: Initial analyte concentration

3.000 mmol Br^- in (5.000 + 25.00) mL gives 0.1000 M Br^-

pAg^+ = ? “Indeterminant”

Region 2: Before equivalence point – analyte in excess

Titration reaction: $Br^-_{(aq)} + Ag^+_{(aq)} \Leftrightarrow AgBr_{(s)}$

For the titration reaction $K_{eq} = 1/K_{sp} = 2.0 \times 10^{12}$
… so the reaction has a strong driving force.

a) assume all titrant reacts with analyte
b) Ag^+ comes from dissociation of precipitate

Region 3: Equivalence Point

Titration reaction: $Br^-_{(aq)} + Ag^+_{(aq)} \Leftrightarrow AgBr_{(s)}$

For the titration reaction $K_{eq} = 1/K_{sp} = 2.0 \times 10^{12}$
… so the reaction has a strong driving force.

a) assume all titrant reacts with analyte $Br^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgBr_{(s)}$
b) Ag^+ comes from dissociation of precipitate K_{sp} problem

Region 4: After Equivalence Point

Titration reaction: $Br^-_{(aq)} + Ag^+_{(aq)} \Leftrightarrow AgBr_{(s)}$

For the titration reaction $K_{eq} = 1/K_{sp} = 2.0 \times 10^{12}$
… so the reaction has a strong driving force.
a) assume stoichiometric amount of titrant reacts with analyte
b) Ag^+ comes from excess titrant

For the titration of 5.000 mL of 0.6000 M Br^-, to which we add 25.00 mL of deionized water, with 0.1000 M Ag^+ titrant, calculate pAg:

a) After 1.00 mL of titrant has been added

before equiv pt.; excess Br^-

b) After 29.00 mL of titrant has been added

before equiv pt.; excess Br^-

c) After 30.00 mL of titrant has been added

at equiv pt.; $[Ag^+] = \sqrt{K_{sp}}$

d) After 30.02 mL of titrant has been added

after equiv pt.; $[Ag^+]$ = mol excess Ag^+ / total vol

e) After 31.00 mL of titrant has been added

after equiv pt.; $[Ag^+]$ = mol excess Ag^+ / total vol

==

a) added 1.00 mL of titrant Ag^+

1) Where on titration curve? What is in excess?

2) Calculate the concentration of excess species assuming all titrant reacted

$[Br^-]$ = (total mol of Br^- - mol Ag^+ added)/(total solution volume)
$[Br^-]$ = (5.000 mL × 0.6000 M - 1.00 mL × 0.1000 M)/(5.000 + 25.00 + 1.00 mL)
= 0.0935_5 M

3) Calculate the concentration of the monitored species (Ag^+)

- Titration reaction: $Br^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgBr_{(s)}$
- Back (or reverse) reaction: $AgBr_{(s)} \Leftrightarrow Br^-_{(aq)} + Ag^+_{(aq)}$
- The reverse reaction is the only source of Ag^+.

$[Ag^+] = K_{sp}/[Br^-] = 5.0 \times 10^{-13} / 0.0935_5\text{ M} = 5.3_{45} \times 10^{-12}\text{ M}$
$pAg = -\log [Ag^+] = 11.27_{21}$

b) added 29.00 mL of titrant

1)Where on titration curve? What is in excess?

2)Calculate the concentration of the excess species assuming all titrant reacted

$[Br^{-}]$ = (total mol of Br^{-} - mol Ag^{+} added)/ (total solution volume)
$[Br^{-}]$ = (5.000 mL × 0.6000 M - 29.00 mL × 0.1000 M)/(30.00 + 29.00 mL)
= $1.694_9 \times 10^{-3}$ M

3) Determine the concentration of the monitored species (Ag^{+})

- Back (or reverse) reaction: $AgBr_{(s)} \rightarrow Br^{-}_{(aq)} + Ag^{+}_{(aq)}$
- The reverse reaction is the only source of Ag^{+}

$[Ag^{+}] = K_{sp}/[Br^{-}] = 5.0 \times 10^{-13} / 1.694_9 \times 10^{-3}$ M $= 2.9_{500} \times 10^{-10}$ M
pAg = - log $[Ag^{+}]$ = 9.53_{018}

c) added 30.00 mL of titrant

1)Where on titration curve? What is in excess?

2)Calculate the concentration of the species assuming all titrant reacted

$[Ag^{+}] = \sqrt{(K_{sp})} = \sqrt{(5.0\text{x}10\text{-}^{13})} = 7.0_{71} \text{ x } 10^{-7}$ M
pAg^{+} = -log[Ag+] = log(7.0_{71}x10-^{7} M) = 6.15_{05}

d) added 30.02 mL of titrant

1)Where on titration curve? What is in excess?

2)Calculate the concentration of the excess species assuming all analyte reacted

$[Ag^{+}]$ = (total mol of Ag^{+} - mol Br^{-} initially)/total solution volume
$[Ag^{+}]$ = (30.02 mL × 0.1000 M - 5.000 mL × 0.6000 M)/(60.02 mL)
= $3.332_2 \times 10^{-5}$ M
pAg = - log $[Ag^{+}]$ = 4.4772_7 or **pAg = 4.4773**

e) added 31.00 mL of titrant

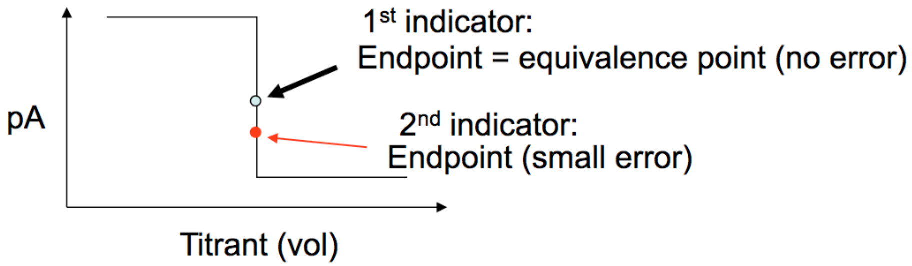
1)Where on titration curve? What is in excess?

2)Calculate the concentration of the excess species assuming all analyte reacted

$[Ag^{+}]$ = (total mol of Ag^{+} - mol Br^{-} initially)/new solution volume
$[Ag^{+}]$ = (31.00 mL × 0.1000 M - 5.000 mL × 0.6000 M)/(61.00 mL)
= $1.639_3 \times 10^{-3}$ M
pAg = - log $[Ag^{+}]$ = 2.7853_4 or **pAg = 2.7853**

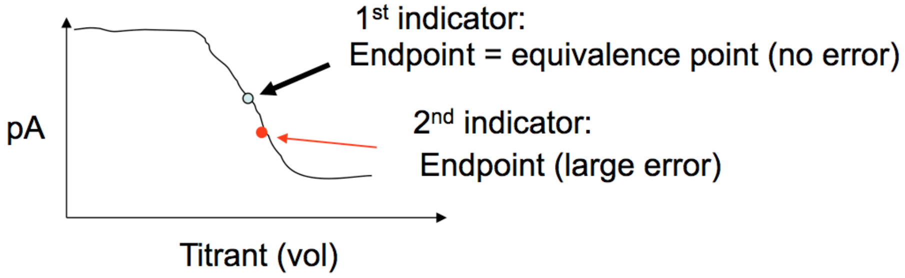
Endpoint in precipitation titration

In titration, we want to have a sharp change or very small $\Delta V_{titrant}$ near the equivalence point.



1st indicator:
Endpoint = equivalence point (no error)

2nd indicator:
Endpoint (small error)



1st indicator:
Endpoint = equivalence point (no error)

2nd indicator:
Endpoint (large error)

Effect of analyte concentration on sharpness

Titration reaction: $I^-_{(aq)} + Ag^+_{(aq)} \Leftrightarrow AgI_{(s)}$

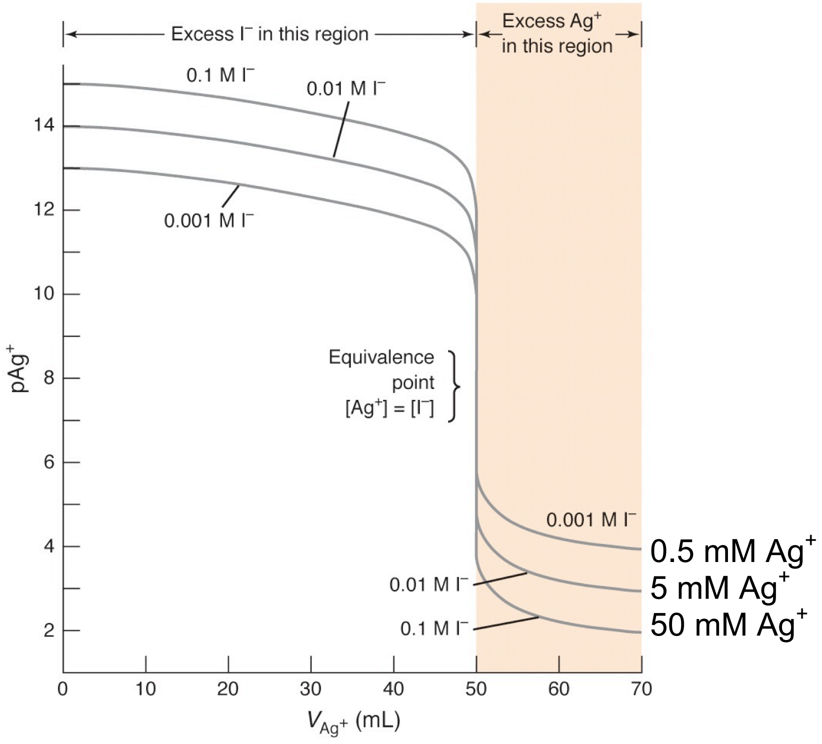
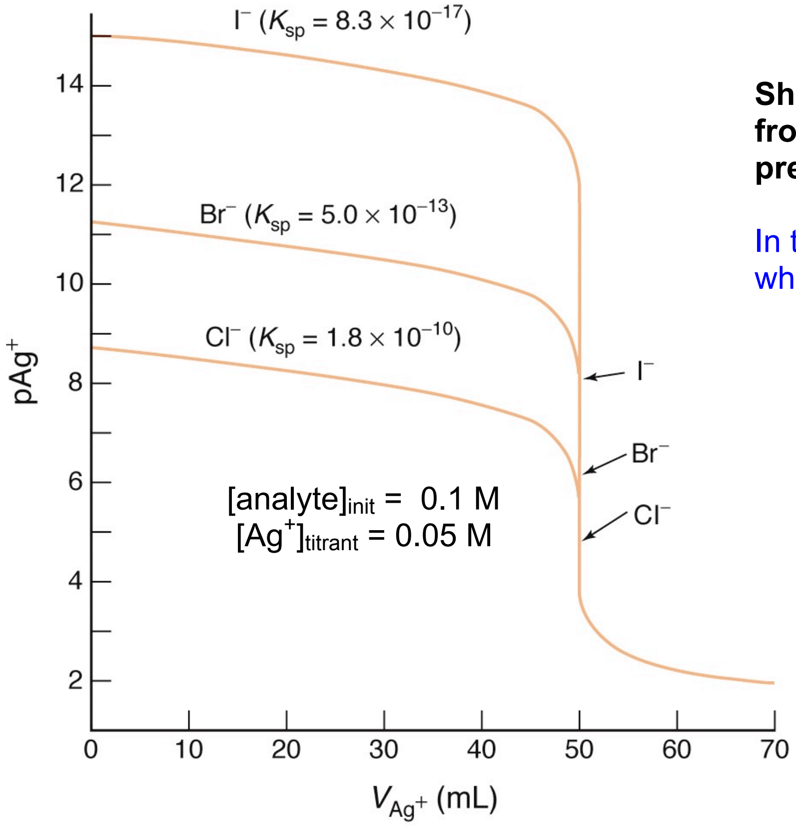


Fig 26-8



Should we care about the $[Ag^+]$ from dissolution of the precipitates?

In theory can ignore reverse reaction when K_{eq} for the titration rxn ≥ 10^8.

Endpoint Detection in Precipitations

- There are several methods available for detecting the endpoint of precipitation titration.

  Chemical indicator – color change
  Light scattering
  Potentiometric measurements - e.g. Ag^+ sensitive electrodes
  Amperometric detection

- Chemical indicator method is commonly used for ppt titrations.

  The color change should occur over a limited range of titrant volume, i.e., the color change should take place within the steep portion of the titration curve for the analyte (at or near the equivalence point).

Adsorption indicators: the Fajans method.

Surface adsorption of a dye occurs when the charge on the precipitating particles changes at the equivalence point (Harris, Color Plate 33: Fajans titration of Cl^- with $AgNO_3$, using dichlorofluorescein).

This method allows us to perform a direct titration

indicator before titration

indicator adsorbed on precipitate after endpoint

The dichlorofluoresceinate anion, competes with chloride ions, for adsorption on the surface of precipitated silver chloride.

In the first stages of a titration, chloride ions in solution are adsorbed preferentially on the surface of the precipitate.

After the equivalence point:
- chloride ion concentration is very low;
- an excess of the silver ion present helps with the adsorption of dichlorofluoresceinate anion onto the surface of the precipitate.

In acidic solutions dichlorofluoresceinate is not a satisfactory indicator because, being the anion of a weak acid, it forms protonated species that will not function as an indicator. Therefore buffer is often added to control the pH during the titration.

Volhard endpoint method (This method uses a back titration)

Add excess Ag^+ reagent and then

1) Remove the AgCl precipitate by filtration, using care to quantitatively transfer any remaining Ag^+ in solution;

2) Titrate remaining Ag^+ with SCN^- with added trace Fe^{3+} as an indicator.

Titration rxn: $Ag^+ + SCN^- = AgSCN_{(s)}$
Indicator rxn: $Fe^{3+} + SCN^- = FeSCN^{2+}$

- Prior to development of Fajans method this was commonly used. We see how the lack of a good endpoint detection method forced the use of a back titration.

Applications of ppt titrations

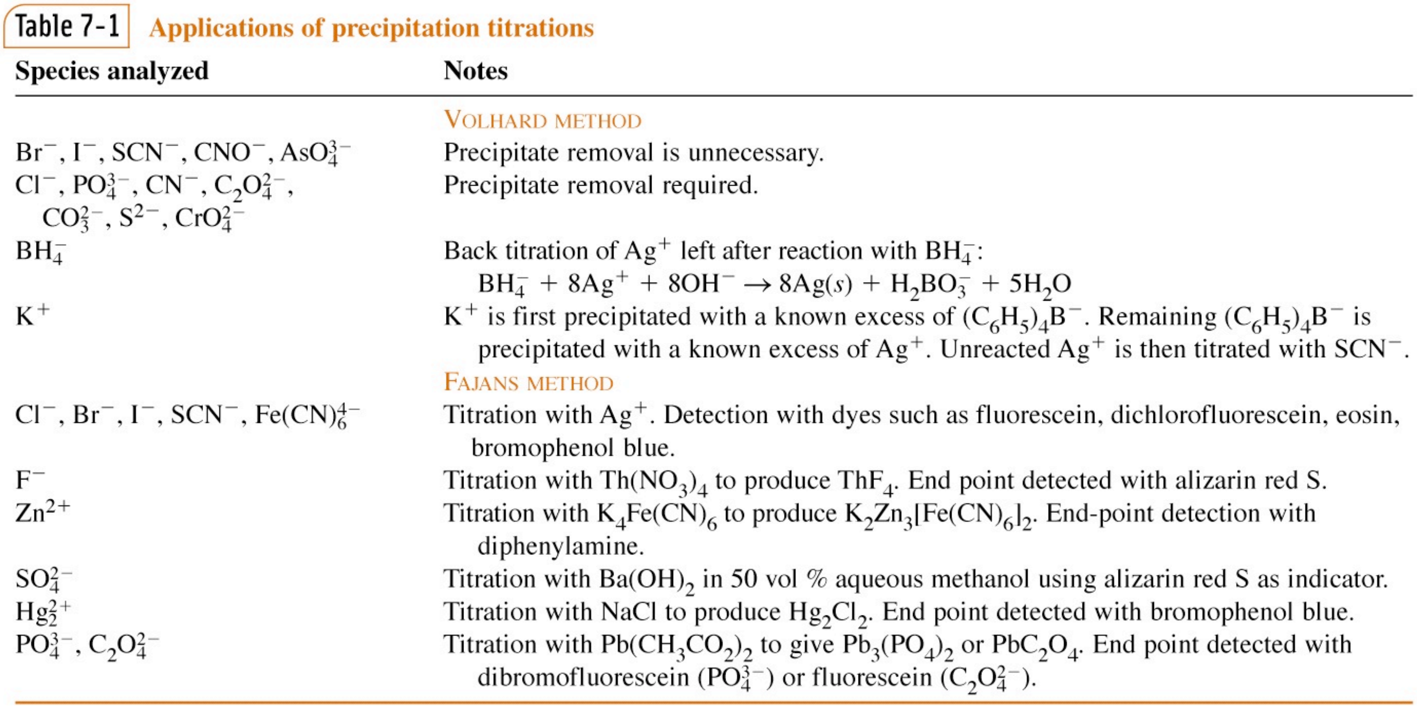


Table 7-1 Applications of precipitation titrations

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 ($C_2O_4^{2-}$).