Precipitation Titrimetry

- Precipitation titrimetry, which is based upon reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques, dating back to the mid-1800s.

- The slow rate of formation of most precipitates, however, limits the number of precipitating agents that can be used in titrimetry to a handful.

- By far the most important precipitating reagent is $AgNO_3$.

- $NaC\ell$ is used as the primary standard for the standardization of $AgNO_3$ solution.

Single anion

Calculate the pAg of the solution during the titration of 50.00 mL of 0.0500 mol L^{-1} NaCℓ with 0.1000 mol L^{-1} $AgNO_3$ after the addition of the following volumes of reagent: (a) 0.00, (b) 24.50, (c) 25.00 and (d) 25.50 mL. (K_{sp} = 1.82 x 10^{-10})

$$Ag^+_{(aq)} + C\ell^-_{(aq)} \rightleftharpoons AgC\ell_{(s)}$$

(a) Because no $AgNO_3$ has been added, $[Ag^+]$ = 0 and pAg is indeterminate.

(b) At 24.50 mL added, $[Ag^+]$ is very small and cannot be computed from stoichiometric considerations alone but $[C\ell^-]$ can still be obtained directly.

$$c_{NaCl} = \frac{n_{NaCl_{initial}} - n_{AgNO_{3added}}}{V_{total}} = [Cl^-]$$

pAg = 6.57

$$[Ag^+] = 2.71x10^{-7}\ mol\ L^{-1}$$

(c) This is the equivalence point where $[Ag^+] = [C\ell^-]$ and

$$[Ag^+] = [Cl^-]$$

pAg = 4.87

$$[Ag^+] = 1.349x10^{-5}\ mol\ L^{-1}$$

(d) The solution now has as and excess of Ag^+. Therefore,

$$[Ag^+] = c_{AgNO_3} = \frac{n_{AgNO_{3added}} - n_{NaCl_{initial}}}{V_{total}} = 6.62x10^{-4}\ mol\ L^{-1}$$

pAg = 3.18

Effect of tritant concentration

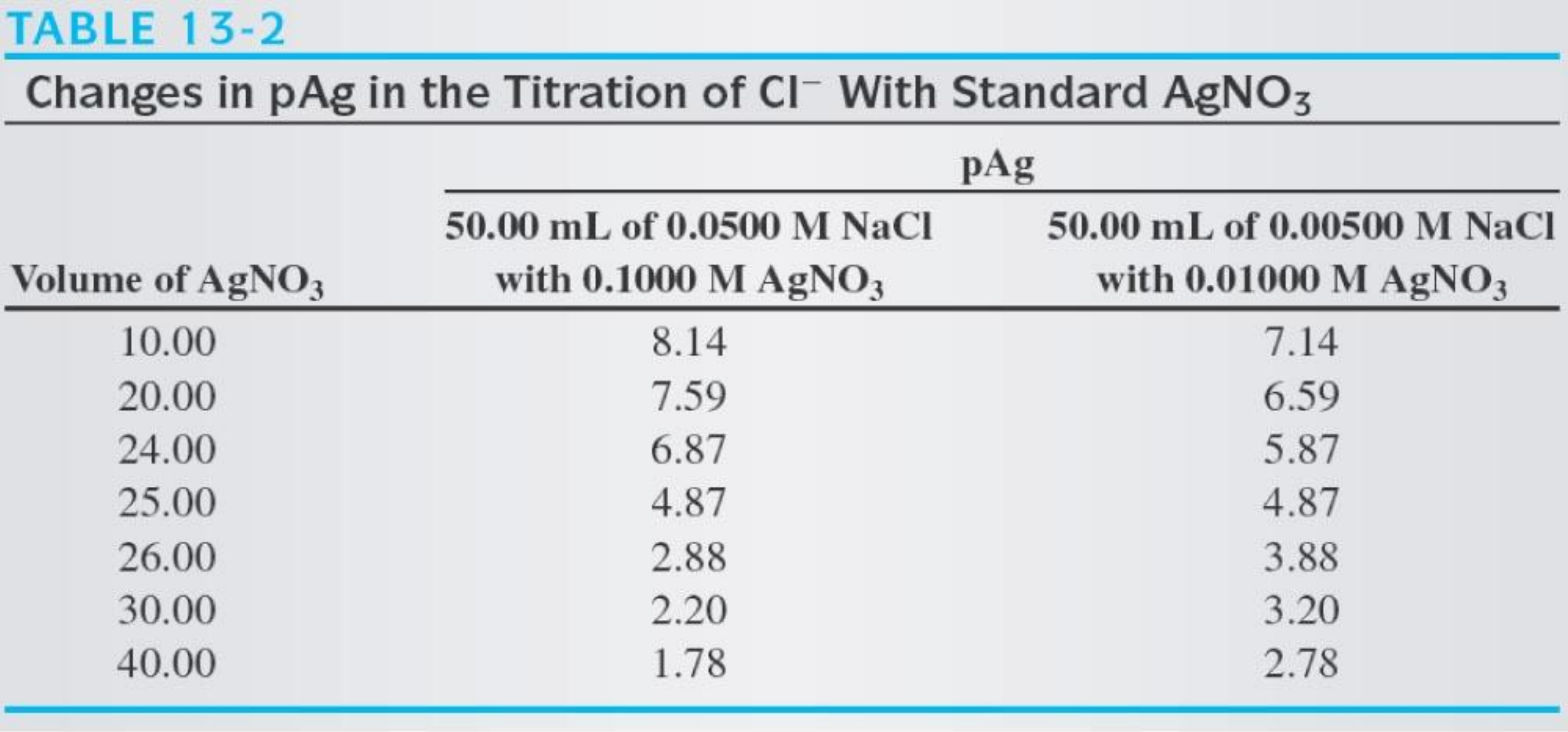
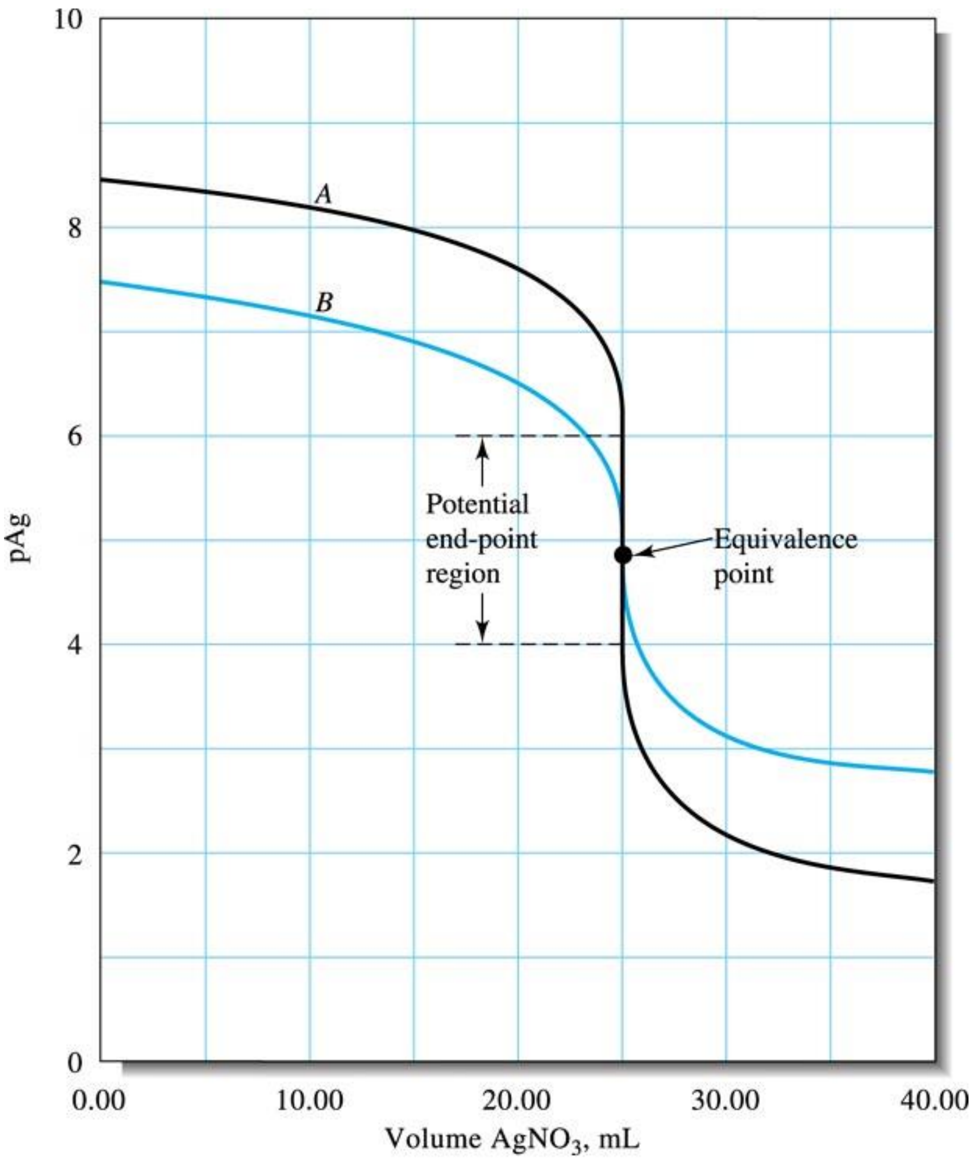


TABLE 13-2

Changes in pAg in the Titration of Cl^- With Standard $AgNO_3$

	pAg	
Volume of $AgNO_3$	**50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$**	**50.00 mL of 0.00500 M NaCl 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

A B



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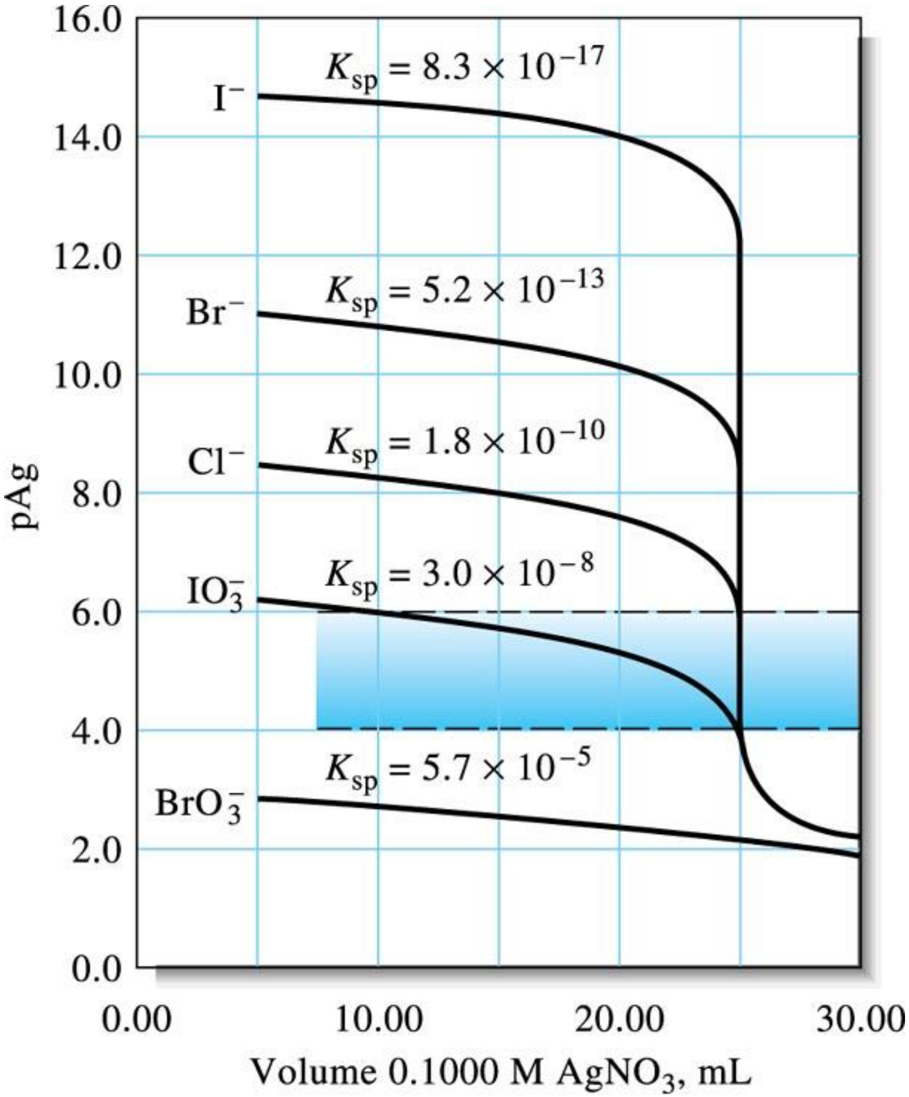
Curve A – the change in pAg in the equivalence-point region is large.

Curve B – the change is markedly less but still pronounced.

Indicator - pAg range of 4 and 6 – should provide a sharp end point in the titration of the 0.05 mol L^{-1} chloride solution (curve A)

For the more dilute solution → the end point would be drawn out over a large enough volume of reagent to make accurate establishment of the end point impossible (curve B).

Effect of solubility product



Effect on the sharpness of the end point.

The change in pAg at the equivalence point becomes greater as the solubility products become smaller.

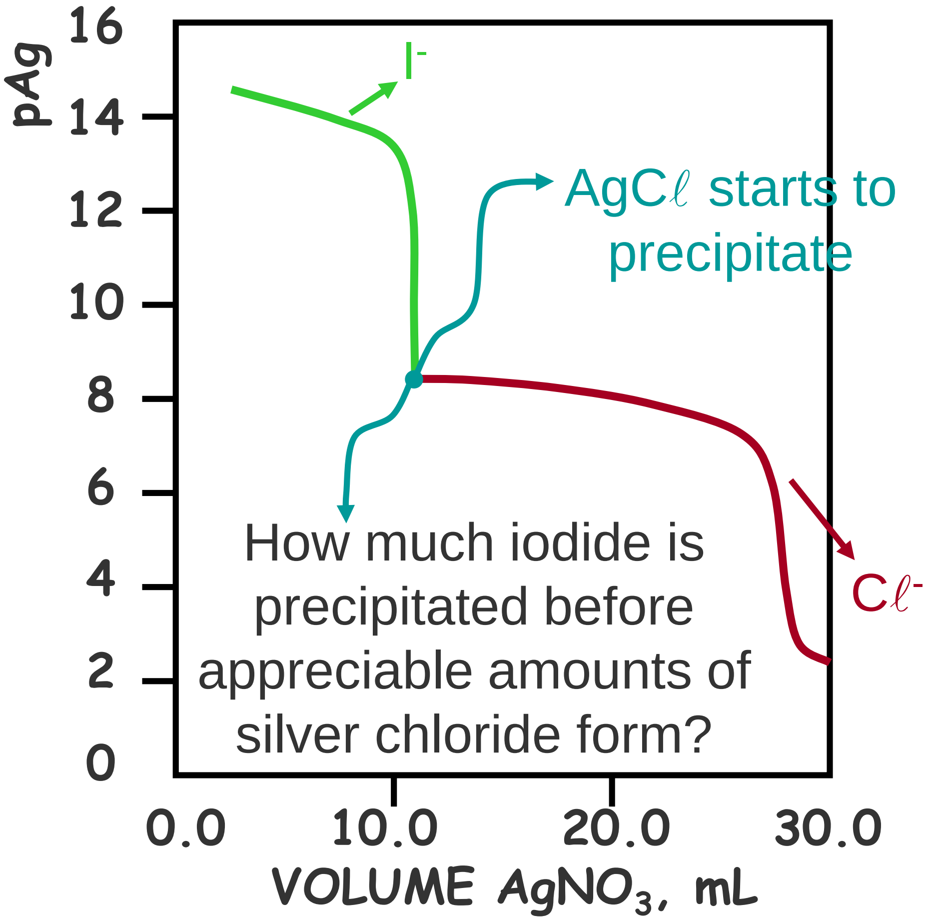
Ions forming precipitates with solubility products much larger than about 10^{-10} do not yield satisfactory end points.

Mixtures of Anions

$C\ell^-$ and I^-

K_{sp} AgCℓ = 1.8×10^{-10}

K_{sp} AgI = 8.3×10^{-17}



AgCℓ starts to precipitate

How much iodide is precipitated before appreciable amounts of silver chloride form?

The curve for the initial stages of this titration is identical to curve for iodide, because silver chloride, with its much larger solubility product, does not begin to precipitate until well into the titration.

To illustrate, consider the titration of 50.00 mL of a solution that is 0.0500 mol L^{-1} in iodide ion and 0.0800 mol L^{-1} in chloride ion with 0.1000 mol L^{-1} silver nitrate.

How much iodide is precipitated before appreciable amounts of silver chloride form?

With the appearance of the smallest amount of solid silver chloride, the solubility-product expressions for both precipitates apply, and division of one by the other provides the useful relationship

$$\frac{[\cancel{Ag^{+}}][I^{-}]}{[\cancel{Ag^{+}}][Cl^{-}]} = \frac{8.3x10^{-17}}{1.8x10^{-10}} = 4.6x10^{-7}$$

For all practical purposes, formation of silver chloride will occur only after 25.00 mL of titrant have been added in this titration. At this point because of dilution, the chloride ion concentration is approximately

$$c_{Cl} = [Cl^-] = \frac{V_{Cl^-} x [Cl^-]}{V_{total}} = 0.0533 mol\, L^{-1}$$

$$[I^-] = 2.45x10^{-8}\, mol\, L^{-1}$$

The iodide concentration is decreased to a tiny fraction of the chloride ion concentration prior to the onset of silver chloride precipitation.

The percentage of iodide unprecipitated at this point can be calculated as follows:

$$n_{I^-} = 75.00x2.45x10^{-8} = 1{,}84x10^{-6}\, mol$$

$$n_{I^-\, initial} = 50.00x0.0500 = 2.50\, mol$$

$$\boxed{I^-_{unprecipitated} = \frac{1.84x10^{-6}}{2.50} x100 = 7.4x10^{-5}\%}$$

Thus, to within about 7.4x10^{-5} percent of the equivalence point for iodide, no silver chloride forms, and up to this point, the titration curve is indistinguishable form that for iodide alone.

As chloride ion begins to precipitate...

$$[Ag^+] = \frac{1.8x10^{-10}}{0.0533} = 3.4x10^{-9}\ mol\ L^{-1}$$

pAg = 8.47

V_{added} = 30.00 mL → additions of $AgNO_3$ decrease the chloride ion concentration, and the curve then becomes that for the titration of chloride by itself.

$$c_{Cl} = [Cl^-] = \frac{V_{Cl^-} x[Cl^-] + V_{I^-}[I^-] - V_{AgNO_3}[AgNO_3]}{V_{total}} = 0.0438 mol\ L^{-1}$$

$$[Ag^+] = 4.1x10^{-9}\ mol\ L^{-1}$$

pAg = 8.39

The remainder of the curve can be derived in the same way as a curve for chloride by itself.

Problem

A 1.998-g sample containing $C\ell^-$ and $C\ell O_4^-$ was dissolved in suficient water to give 250.0 mL of solution. A 50.00-mL aliquot required 13.97 mL of 0.08551 mol L^{-1} $AgNO_3$ to titrate $C\ell^-$. A second 50.00-mL aliquot was treated with $V_2(SO_4)_3$ to reduce the $C\ell O_4^-$ to $C\ell^-$:

$$C\ell O_4^- + 4V_2(SO_4)_3 + 4H_2O \rightarrow C\ell^- + 12SO_4^{2-} + 8VO^{2+} + 8H^+$$

Titration of the reduced sample required 40.12 mL of the $AgNO_3$ solution. Calculate the percentages of $C\ell^-$ and $C\ell O_4^-$ in the sample.

Argentometric methods

Determination of:

- Halides ($C\ell^-$, Br^-, I^-)
- Halide-like anions (SCN^-, CN^-, CNO^-)
- Mercaptans
- Fatty acids

End points for argentometric titrations

Chemical

Consists of a color change or, occasionally, the appearance or disapperance of turbidity in the solution being titrated.

Requirements:

1) The color change should occur over a limited range in p-function of the reagent or the analyte;
2) The color change should take place within the steep portion of the titration curve for the analyte.

Instrumental

Potenciometric (by measuring the potential between a silver electrode and a reference electrode whose potential is constant and independent of the added reagent)

Amperometric (the current generated between a pair of silver microelectrodes in the solution of the analyte is measured and plotted as a function of reagent volume)

The Mohr Method

Sodium chromate can serve as an indicator for the argentometric determination of $C\ell^-$, Br^-, and CN^- ions by reacting with silver ion to form a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region.

$$Ag^+ + C\ell^- \rightleftharpoons AgC\ell(s) \text{ (white)}$$

$$2Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4(s) \text{ (red)}$$

$$[Ag^+] = \sqrt{K_{sp}} = 1.35x10^{-5}\ mol\ L^{-1}$$

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

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.2x10^{-12}}{(1.35x10^{-5})^2} = 6.6x10^{-3}\ mol\ L^{-1}$$

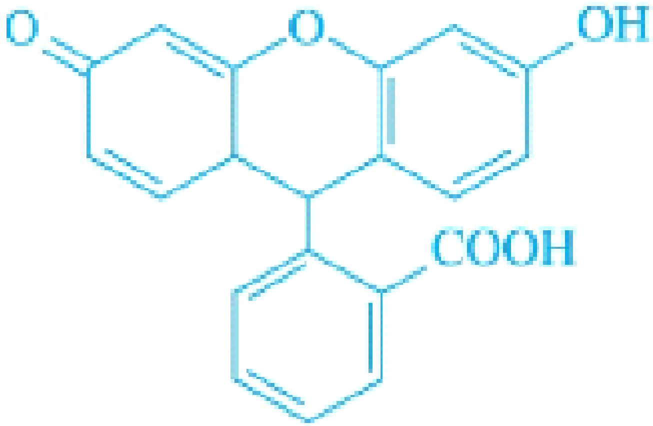
In principle, then, an amount of chromate ion to give this concentration should be added for appearance of the red precipitate just after the equivalence point. In fact, however, a chromate ion concentration of 6.6x10^{-3} mol L^{-1} imparts such an intense yellow color to the solution that formation of the red silver chromate is not readily detected; for this reason, lower concentrations of chromate ion are generally used. An additional excess of the reagent must also be added to produce enough silver chromate to be seen. These two factors create a positive systematic error in the Mohr method that becomes significant in magnitude at reagent concentrations lower than about 0.1 mol L^{-1}. → Blank titration

The Mohr titration must be carried out at a pH between 7 and 10 because chromate ion is the conjugate base of the weak chromic acid.

Consequently, in more acid solutions the chromate ion concentration is too low to produce the precipitate at the equivalence point. Normally, a suitable pH is achieved by saturating the analyte solution with sodium hydrogen carbonate.

Adsorption indicators – The Fajans Method

Adsorption indicator: is an organic compound that ends to be adsorbed onto the surface of the solid in a precipitation titration. Ideally, the adsorption (or desorption) occurs near the equivalence point and results not only in a color change but also in a transfer of color form the solution to the solid (or the reserve).

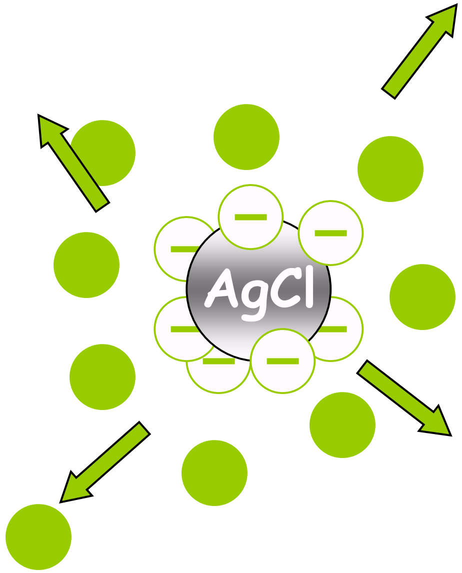


fluorescein

Example: fluorescein → in aqueous solution, fluorescein partially dissociates into hydronium ions and negatively charged fluoresceinate ions that are yellow-green. With Ag^+ → intensely red.

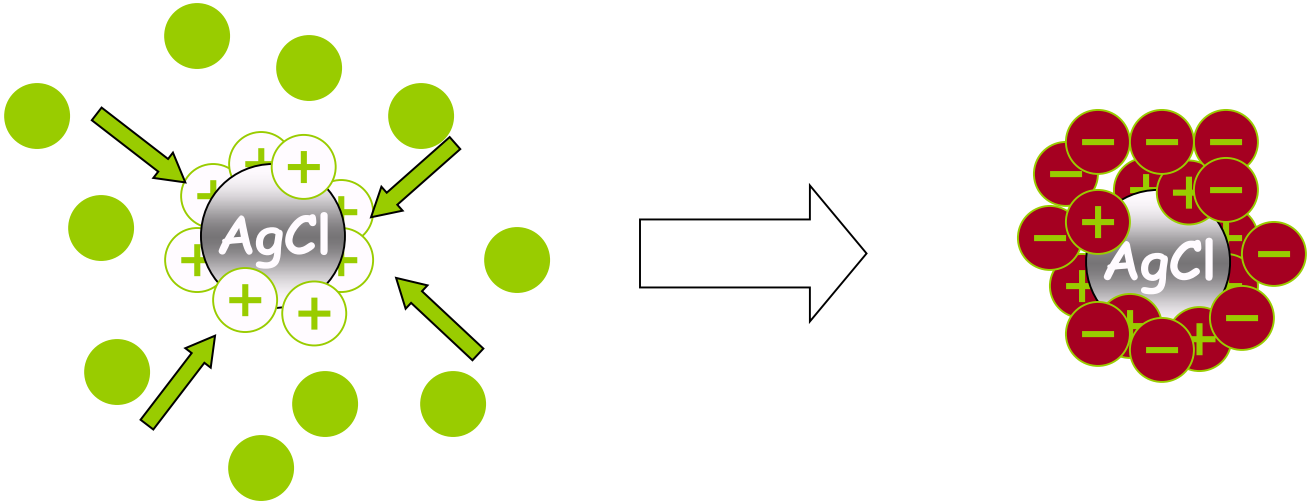
In the early stages of the titration of chloride ion with silver nitrate, the colloidal silver chloride particles are negatively charged because of surface adsorption of excess chloride ions.

The dye anions are repelled from this surface by electrostatic repulsion and impart a yellow-green color to the solution.



Beyond the equivalence point, however, the silver chloride particles strongly adsorb silver ions and thereby acquire a positive charge.

Fluoresceinate anions are now attracted into the counter-ion layer that surrounds each colloidal silver chloride particle. The net result is the appearance of the red color of silver fluoresceinate in the surface layer of the solution surrounding the solid.



The color change → adsorption process → K_{sp} of silver fluoresceinate is never exceeded

The adsorption is reversible: the dye being desorbed upon back-titration with chloride ion.

Titrations involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the relatively few precipitation reactions in which a colloidal precipitate is formed rapidly.

Adsorption indicators – The Fajans Method

Before addition of Ag^+

Adsorption indicators – The Fajans Method

Before addition of Ag^+

After a tiny addition

Adsorption indicators – The Fajans Method

Before addition of Ag^+

After a tiny addition

Near equivalence point

Adsorption indicators – The Fajans Method

Before addition of Ag^+

After a tiny addition

Near equivalence point

End point

Iron(III) ion – The Volhard Method

In the Volhard method, silver ions are titrated with a standard solution of thiocyanate ion:

$$Ag^+ + SCN^- \rightleftharpoons AgSCN(s)$$

Iron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion:

$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+}$

$$K_f = 1.05x10^3 = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

The titration must be carried out in acidic solution to prevent precipitation of iron(III) as the hydrated oxide.

Iron(III) ion – The Volhard Method

The most important application of the Volhard method is for the indirect determination of halide ions.

A measured excess of standard silver nitrate solution is added to sample, and the excess silver ion is determined by back-titration with a standard thiocyanate solution.

The strong acid environment required for the Volhard procedure representes a distinct advantage over the titrimetric methods of halide analysis because such ions as carbonate, oxalate, and arsenate do not interfere.

Negative error → $AgC\ell$ is more soluble than $AgSCN$

$AgC\ell(s) + SCN^- \rightleftharpoons AgSCN(s) + C\ell^-$

- This reaction causes the end point to fade and results in an overconsumption of thiocyanate ion, which in turns leads to low values for the chloride analysis.

- This error can be circumvented by filtering the silver chloride before undertaking the back-titration.

- Filtration is not required in the determination of other halides because they all form silver salts that are less soluble than silver thiocyanate.

Applications

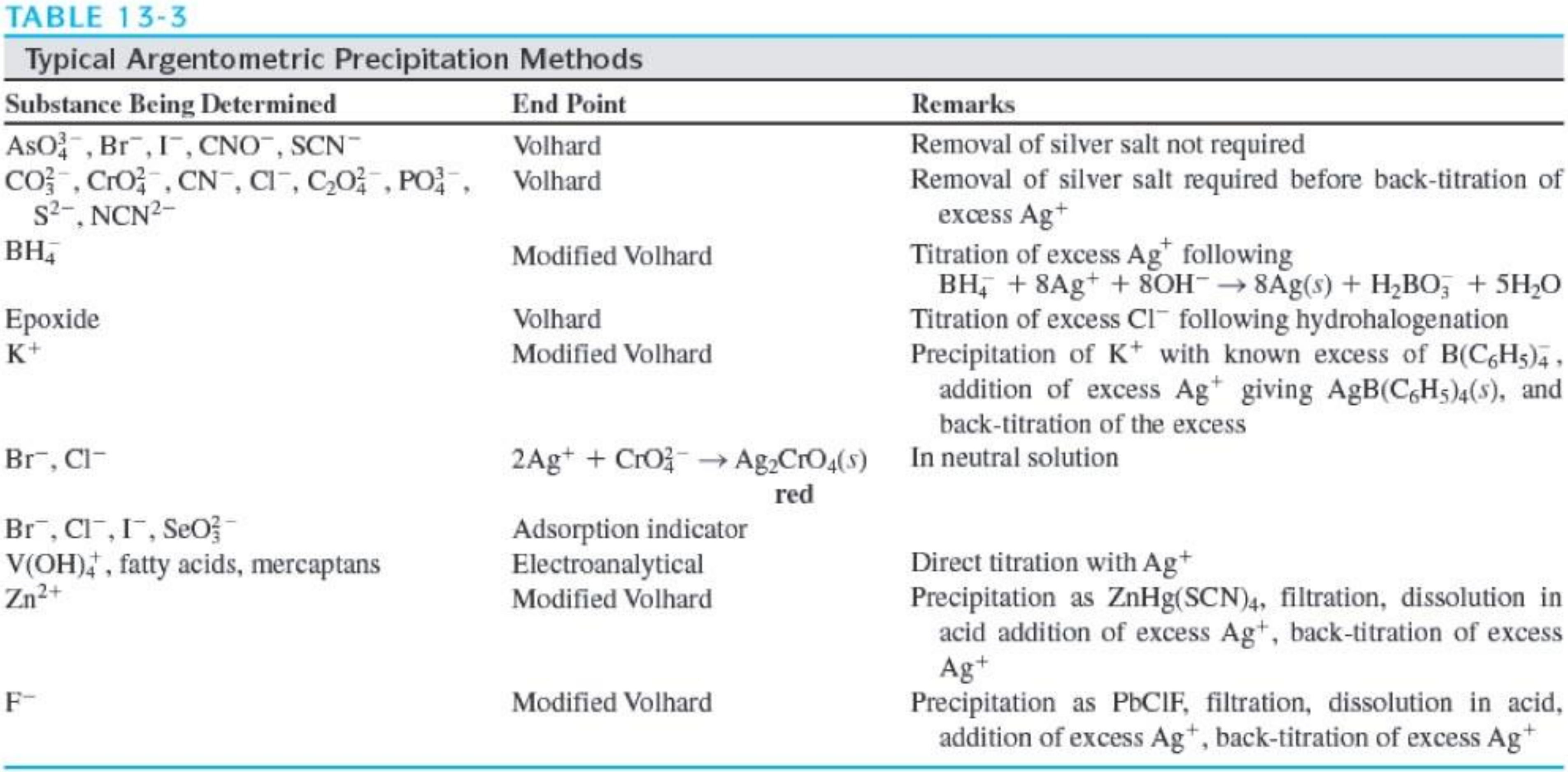


TABLE 13-3

Typical Argentometric Precipitation Methods

Substance Being Determined	End Point	Remarks
AsO_4^{3-}, Br^-, I^-, CNO^-, SCN^-	Volhard	Removal of silver salt not required
CO_3^{2-}, CrO_4^{2-}, CN^-, Cl^-, $C_2O_4^{2-}$, PO_4^{3-}, S^{2-}, NCN^{2-}	Volhard	Removal of silver salt required before back-titration of excess Ag^+
BH_4^-	Modified Volhard	Titration of excess Ag^+ following $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$
Epoxide	Volhard	Titration of excess Cl^- following hydrohalogenation
K^+	Modified Volhard	Precipitation of K^+ with known excess of $B(C_6H_5)_4^-$, addition of excess Ag^+ giving $AgB(C_6H_5)_4(s)$, and back-titration of the excess
Br^-, Cl^-	$2Ag^+ + CrO_4^{2-} \rightarrow \underset{\textbf{red}}{Ag_2CrO_4(s)}$	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^+

Exemplo

The arsenic in a 9.13-g sample of pesticide was converted to AsO_4^{3-} and precipitated as Ag_3AsO_4 with 50.00 mL of 0.02105 mol L^{-1} $AgNO_3$. The excess Ag^+ was then titrated with 4.75 mL of 0.04321 mol L^{-1} KSCN. Calculate the percentage of As_2O_3 (W. M. = 198.4 g mol^{-1}) in the sample.

$$n_{AgNO_3} = 50.00x0.02105 = 1.0525 mmol\,L^{-1}$$

$$n_{SCN^-} = 4.75x0.04321 = 0.2052 mmol\,L^{-1}$$

$$n_{Ag^+ reacted} = 0.8473 mmol\,L^{-1}$$

$As_2O_3 \equiv 2\,AsO_4^{3-} \equiv 6\,AgNO_3$

$$n_{As_2O_3} = \frac{n_{AgNO_3}}{6} = 0.1412\,mmol\,L^{-1} \rightarrow m = 0.0280\,g\,(0.31\%)$$

Problem

The phosphate in a 4.258-g sample of plant food was precipitated as Ag_3PO_4 through the addition of 50.00 mL of 0.0820 mol L^{-1} $AgNO_3$:

$3Ag^+ + HPO_4^{2-} \rightleftharpoons Ag_3PO_4(s) + H^+$

The solid was filtered and washed, following which the filtrate and washings were diluted to exactly 250.0 mL. Titration of a 50.00-mL aliquot of this solution required a 4.64-mL back-titration with 0.0625 mol L^{-1} KSCN. Express the results of this analysis in terms of the percentage of P_2O_5.