Precipitation titrimetry

Gábor Galbács

This is one of the oldest methods of analytical chemistry. It is a volumetric titration method where the reaction between the titrant and sample solutions yield precipitate (low solubility, usually ionic compounds).

But is it possible at all to develop a titrimetric method based on precipitation reactions?

- the formation of precipitate can be stoichiometric
- the reaction can be quantitative
- precipitate formation is usually slow
- evolving of the reaction is apparent, but the end-point is obscured, hazy...
**Argentometry**

Argentometry, where the titrant is a standard AgNO₃ solution is the most common precipitation titrimetric method, because

- silver precipitates are usually highly insoluble
- many species form stoichiometric precipitates with Ag⁺ (e.g. Cl⁻, Br⁻, I⁻, F⁻, CN⁻, SCN⁻, CrO₄²⁻, PO₄³⁻, AsO₄³⁻, etc.)
- these precipitates are formed quickly

Examples:

\[ K_{sp, AgCl} = 1.8 \times 10^{-10} \]
\[ K_{sp, AgBr} = 5.2 \times 10^{-13} \]
\[ K_{sp, AgI} = 8.3 \times 10^{-17} \]
\[ K_{sp, AgSCN} = 4.9 \times 10^{-13} \]

**Argentometry - standardization**

Titrant is a standardized AgNO₃ solution. It is not a primary standard, because silver ions are easily reduced to elemental Ag, e.g. they are also *light sensitive*. The titrant needs to be stored in a dark (brown) container and standardization is also needed.

The standardization is done by a standard alkali-halide solution (e.g. NaCl, KCl)

\[ Ag^+ + NO_3^- + Na^+ + Cl^- \rightarrow AgCl + NO_3^- + Na^+ \]
**Argentometric titration curves**

In argentometry, the titration curves usually plot pAg against the added titrant volume. Note, that an increasing pAg means strongly decreasing [Ag⁺]. During the titration, the precipitate equilibrium determines pAg.

Example: 50 mL 0.1 M KSCN sample 0.1 M AgNO₃ titrant

\[ K_{sp,AgSCN} = 4.9 \times 10^{-13} \]

*Before the equivalence point:*

pAg is controlled by the remaining SCN⁻ concentration

*At the equivalence point:*

pAg can be directly calculated from \( K_{sp} \)

*After the equivalence point:*

pAg is controlled by the excess Ag⁺

---

**Titration of KSCN with AgNO₃**

Before the equivalence point

0 mL titrant added (0%): pAg can not be calculated, as Ag⁺ is not present in sample...

\[ K_{sp} = [Ag^+] \times [SCN^-] \]

10 mL titrant added (20%):

\[ pAg = -\lg \left( \frac{K_{sp}}{c_{SCN\text{-remaining}}} \right) \]

because solubility is neglectable...

\[ c_{SCN\text{-remaining}} = \left( c_{KSCN, \text{total}} \cdot V_{KSCN} - (c_{AgNO₃} \cdot V_{AgNO₃, \text{added}}) \right) / V_{\text{total}} \]

\[ pAg = -\lg \left( \frac{4.9 \times 10^{-13}}{0.0666 \text{ M}} \right) = 11.13 \]

25 mL titrant added (50%):

\[ pAg = -\lg \left( \frac{4.9 \times 10^{-13}}{0.0333 \text{ M}} \right) = 10.83 \]
**Titration of KSCN with AgNO₃**

**Region 2: At the equivalence point**

50 mL titrant was added (100%):

there is only the precipitate present

\[ \text{pAg} = -\lg(\sqrt{K_{sp}}) \]

\[ \text{pAg} = 6.15 \]

---

**Titration of KSCN with AgNO₃**

**After the equivalence point**

75 mL titrant added (150%):

\[ [\text{Ag}^+] \text{ is controlled by the excess titrant, as the solubility of the precipitate is relatively neglectable} \]

\[ \text{pAg} = -\lg (c_{\text{Ag}^+, \text{excess}}) \]

\[ c_{\text{Ag}^+, \text{excess}} = \frac{(c_{\text{AgNO₃, added}})\cdot(V_{\text{AgNO₃, added}})-(c_{\text{KSCN, total}}\cdot V_{\text{KSCN}}))}{V_{\text{total}}} \]

\[ \text{pAg} = -\lg (0.02 \text{ M}) = 1.69 \]

100 mL titrant added (200%):

\[ \text{pAg} = -\lg (0.033 \text{ M}) = 1.47 \]
Argentometric titration curves

Figure 13-5  Titration curve for the titration of 50.00 mL of 0.1000 M \( \text{AgNO}_3 \) with 0.1000 M \( \text{KSCN} \).

Effect of \( K_{sp} \) on titration curves

Figure 13-5  Effect of reaction completeness on precipitation titration curves. For each curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M \( \text{AgNO}_3 \). Note that smaller values of \( K_{sp} \) give much sharper breaks at the end point.
Measuring halides side by side

Figure 7-8 Experimental titration curves. (a) Titration curve for 40.00 mL of 0.0052 M HBrO₃ plus 0.005 M M. KOH. The inset is an expanded view of the region near the first equivalence point. (b) Titration curve for 25.00 mL of 0.100 M HBrO₃ titrated with 0.0005 M Ba(NO₃)₂.

Figure 13-6 Titration curves for 50.00 mL of a solution 0.0800 M in Cl⁻ and 0.0500 M in I⁻ or Br⁻.
End point detection methods

As was alluded to before, end point detection is crucial for the success of precipitation titrations. The following end-point detection methods are (or has been) used in the practice:

- the Gay-Lussac method
- the Mohr method
- the Volhard method
- the Fajans method
- the instrumental method
End-point detection methods: Gay-Lussac

This approach actually uses no indicator. Instead, the end-point is detected via the point of flocculation. If the titration is performed slowly and carefully, it can be observed that at the end-point, no further precipitate forms as a result of the next droplet of titrant, but the precipitate suddenly flocculates, that is fluffy large agglomerates are formed (the sample solution sort of clears up).

The cause for this flocculation is that precipitate particles tend to adsorb their own ions, especially the one which is in excess (the halide anions before the EP and silver cations after the EP), thereby acquiring electric charge. Because of this, they repel each other. At exactly the EP, there is no excess of ions, so no charge, thus the particles attach to each other (flocculate).

This method is not very reliable. The more insoluble is the precipitate, the better is the accuracy.

End-point detection methods: Mohr

This approach uses chromate ions (CrO₄²⁻) as the indicator. The idea behind the method is that Ag₂CrO₄ is a red precipitate, the solubility of which is somewhat better than that of the silver halide precipitates. Thus, if a calculated amount of chromate ions is added to the sample and the titration commences, as soon as we pass the EP, the excess of silver ions will initiate the precipitation of red Ag₂CrO₄.

The reliability of this method depends largely on the concentration of the indicator anion and the pH, as the latter influences the solubility of the indicator precipitate. Also because of the carcinogenic nature of Cr(VI), this method is seldomly used.
End-point detection methods: **Volhard**

This method is based on back-titration and uses a soluble, intensively colored substance (Fe(III)-thiocyanate complex) as indicator. Silver ions in a known amount, but in excess are added to the sample. All halide ions are precipitated and the remaining free silver ions are then back-titrated using a KSCN solution in the presence of Fe(III) ions. Fe(III) ions form a reddish complex with thiocyanate ions. This color will show as soon as the EP is passed during titration.

\[
\begin{align*}
\text{Ag}^+ + \text{Cl}^- & \rightarrow \text{AgCl(s)} \\
\text{Ag}^+ + \text{SCN}^- & \rightarrow \text{AgSCN(s)} \\
\text{Fe}^{3+} + \text{SCN}^- & \rightarrow \text{FeSCN}^3^- \quad \text{Red}
\end{align*}
\]

This method is reliable, but not very accurate (positive and negative errors can both be present due to the interaction of the two silver precipitates). Accurate measurements can be done, but preventive actions – via the addition of further reagents – are needed.

End-point detection methods: **Fajans**

This method is based on the use of adsorption indicators. Fajans’s idea stems from the fact that at the end-point, the surface charge of silver halide precipitate particles will change polarity.

If indicator anions are added to the sample (e.g. eosin, p-etoxy-chrysoidine, fluorescein), that form a colorful precipitate with silver ions, then these anions can only be adsorbed on the surface of the silver halide precipitate from the end-point on. On the surface, concentration conditions allow the formation of the corresponding precipitate, and hence the color of their appearance allows the end-point detection. For example, fluorescein and eosin gives pink color.
End-point detection methods: Fajans

Dye adsorption makes the silver halide susceptible to photochemical reduction (silver deposition), therefore it is best to perform the titration in dark.

This method is reliable and accurate, but the accuracy depends again on the pH and experiencedness of the analyst.

End-point detection methods: instrumental
Precipitation titrations: some applications

Table 7-1  Applications of precipitation titrations

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(^-), I(^-), SCN(^-), AsO(_4)^{3-}\</td>
<td>Volumetric Method</td>
</tr>
<tr>
<td>CN(^-), PO(_4)^{3-}, C(_2)O(_4)^{2-}, CO(_3)^{2-}, SF(_2), CO(_2)^{2-}\</td>
<td>Precipitate removal is unnecessary.</td>
</tr>
<tr>
<td>BI(_2) | Precipitate removal required.</td>
<td></td>
</tr>
<tr>
<td>K(^+) | Back titration of Ag(^+) left after reaction with BI(_2):</td>
<td></td>
</tr>
<tr>
<td>BI(_2) + KAg(^+) + KOH \rightarrow KAg(s) + H(_2)O + SH(_2)D</td>
<td></td>
</tr>
<tr>
<td>K(^+) is first precipitated with a known excess of (C(_2)H(_2))(_2)B. Remaining (C(_2)H(_2))(_2)B (_2) is precipitated with a known excess of Ag(^+). Unreacted Ag(^+) is then titrated with SCN(^-).</td>
<td></td>
</tr>
<tr>
<td>Fe(CN)(_6)^{3-}\</td>
<td>Fajan's Method</td>
</tr>
<tr>
<td>C(_1), Br(^-), I(^-), SCN(^-), Fe(CN)(_6)^{3-}\</td>
<td>Titrations with Ag(^+): Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromophenol blue.</td>
</tr>
<tr>
<td>Fe(^+) | Titrations with Th(NO(_3))(_4) to produce ThF(_4). End point detected with alizarin red S.</td>
<td></td>
</tr>
<tr>
<td>Ze(_n)^{+}\</td>
<td>Titrations with K(_2)Fe(CN)(_6) to produce K(_2)Zn(Fe(CN)(_6))(_2). End point detected with diphenylamine.</td>
</tr>
<tr>
<td>SO(_4)^{2-}\</td>
<td>Titrations with Ba(OH)(_2) in 50 vol% aqueous methanol using alizarin red S as indicator.</td>
</tr>
<tr>
<td>Hg(_2)^{2+}\</td>
<td>Titrations with NaCl to produce Hg(_2)Cl(_2). End point detected with bromophenol blue.</td>
</tr>
<tr>
<td>PO(_4)^{3-}, C(_2)O(_4)^{2-}\</td>
<td>Titrations with Pb(CH(_3)CO(_3))(_2) to give Pb(_2)(PO(_4))(_3) or PbC(_2)O(_4). End point detected with dichromofluorescein (PO(_4)^{3-}) or fluorescein (C(_2)O(_4)^{2-}).</td>
</tr>
</tbody>
</table>

Checklist for precipitation titrations

Remember:

• the discussed formulas of precipitate equilibria
• effect of concentration and \(K_{sp}\) on the titration curve
• methods of standardization for the AgNO\(_3\) titrant
• end-point detection methods
• potential applications