**Precipitation Titrations**

Precipitation relies on a complete reaction between analyte and precipitating reagent. This is also one of the requirements of a titration reaction. Precipitation reactions are generally slow, involving periods of digestion, cooling, filtration etc. This tends to limit the reactions that are available for titration.

**General Principles**

The major precipitation reaction used is that of silver with a range of anions. These anions include:

- Chloride
- Bromide
- Iodide
- Thiocyanate

Titrations involving silver are termed *argentometric*, from the old name for silver, *argentum*.

The reaction rates for the silver salt precipitation is rapid. The reaction ratio is 1:1 and silver salts formed are generally quite insoluble. Table 6.1 gives the solubility product, $K_{sp}$, for the silver salts that are involved in precipitation titrations.

<table>
<thead>
<tr>
<th>Anion</th>
<th>$K_{sp}$</th>
<th>Solubility (g/100mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>$1.8 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>$5.2 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>I$^-$</td>
<td>$8.3 \times 10^{-17}$</td>
<td></td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>$1.1 \times 10^{-12}$</td>
<td>$0.00002$</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>$2.6 \times 10^{-12}$</td>
<td>$0.0025$</td>
</tr>
</tbody>
</table>

Table 6.1 Solubility products for silver salts

**Exercise 6.1**

Write the equation for the dissolving of each of the species in Table 6.1 and also the equilibrium expression for each.
Exercise 6.2
What does the value for the $K_{sp}$ indicate about the solubility of the solid and also the position of the equilibrium?

Silver Nitrate as Titrant
One of the most important reactions of silver is the formation of solid silver chloride. This titration has widespread uses in the areas of agriculture, food, pathology and water analysis.

Silver nitrate is available in AR grade form, but it is hygroscopic and therefore unable to be used as a primary standard. It can be standardised against dried sodium chloride.

The formation of the precipitate is usually easy to observe, it is not easy to observe when the precipitation ends ie when there is an excess of the titrant. This means that some form of endpoint detection is required. Possibilities include electrical measurements and indicators.

Mohr’s method
Uses potassium chromate as the indicator. Chromate is yellow in neutral and alkaline conditions and at endpoint is more soluble than silver chloride. It will only form after all the chloride has been precipitated.

Errors are introduced due to the need to add excess titrant before the endpoint colour is visible. To overcome this error it is necessary to carry out blank titrations, where only indicator is present. It is also important to use a constant amount (1 mL) of indicator in all titrations.:
- If too little indicator is used the silver concentration must be higher after equivalence point before any precipitation of $\text{Ag}_2\text{CrO}_4$ occurs.
- If too much indicator is used the colour change will be difficult to see due to the intense yellow colour.

Mohr’s method works in the pH region of 6-9 only.
- Above this pH, silver will form a precipitate with hydroxide.
- Below this pH chromate converts to dichromate, a bright orange colour thereby obscuring the endpoint. Calcium carbonate is often added to reduce the acidity of the solution.

Mohr’s method is suitable only for titration of chloride, bromide and cyanide.
**Fajans method**
This method uses an **adsorption indicator** such as fluorescein and eosin. The indicator adsorb onto the surface of the silver salt precipitate at the endpoint. The adsorption process causes a change in the colour of the indicator.

Common Fajans adsorption indicators are weakly acidic organic compounds and in alkaline conditions will exist as the conjugate base, $\text{In}^-$. It is this form of the indicator which interacts with the precipitate.

![Diagram](image)

Fig 6.1 Colloidal silver salts (a) before endpoint and (b) after endpoint

- $\text{AgNO}_3$ added to a dilute solution of $\text{NaCl}$, the solution becomes turbid and if other electrolytes are absent, coagulation does not occur immediately.
- The colloidal sized $\text{AgCl}$ particles **adsorb** $\text{Cl}^-$ and these attract sodium ions as shown in Fig 6.1(a)
- Colloidal particles are electrically charged and repel each other preventing coagulation
- As titration continues, the amount of chloride decreases but there is still some surface charge which acts to repel the negatively charged indicator ion.
- Immediately after endpoint there is an excess of silver ions which will adsorb onto the surface of the precipitate
- The charged surface has now changed polarity and attracts the negative indicator ion
- A colour change will be observed
- A blank titration is not required as the indicator does not react with the titrant

**Limitations of Fajan’s method**
- Low background levels of non-reacting ions to ensure that coagulation does not occur.
- Will not work with very low levels as there will not be enough precipitate to allow the colour change to be observed
- Method is pH dependent as the indicator must be in the ionised form

Fajan’s method can be used to titrate silver with a standard chloride solution. This is not possible in Mohr’s method since chromate added to a silver solution would immediately cause a precipitate.
Common adsorption indicators

<table>
<thead>
<tr>
<th>INDICATOR</th>
<th>COLOUR CHANGE (free to adsorbed)</th>
<th>APPLICATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>Yellow-green to pink</td>
<td>All halides, pH 7-10</td>
</tr>
<tr>
<td>Eosin</td>
<td>Pink to red-violet</td>
<td>Sample must not contain Cl⁻, pH &gt;1</td>
</tr>
<tr>
<td>Diiododimethylfluorescein</td>
<td>Orange to blue</td>
<td>I⁻ only, pH 4-7</td>
</tr>
<tr>
<td>Dichlorofluorescein</td>
<td>Yellow-green to red</td>
<td>Cl⁻ and Br⁻, pH 4-7</td>
</tr>
</tbody>
</table>

**Potassium Thiocyanate as Titrant (Volhard’s method)**

This method uses a back titration with potassium thiocyanate and is suitable for the determination of chlorides, bromides and iodides in acidic solutions. A known excess of silver nitrate solution is added to the sample and the excess is back titrated with standard thiocyanate solution. The titration uses iron III as the indicator.

The iron III indicator works by forming the coloured complex when an excess of thiocyanate occurs. The solution must be acidic, with a concentration of about 1 M in nitric to ensure the complex formed is stable.

The method is suitable for the direct determination of silver or for the indirect determination of halide ions.

An error is introduced in the method for the analysis of chloride as AgCl is more soluble than AgSCN ie some of the AgCl precipitate will redissolve by reacting with the thiocyanate titrant. This can be overcome by:

- Filtering off the precipitate prior to titration…..but this leads to transfer errors
- Adding nitrobenzene which forms an impervious coating on the AgCl precipitate preventing it reacting with the thiocyanate. (About 1 mL nitrobenzene per 50 mg of chloride).

Thiocyanate is standardised against a standard silver solution, with the silver solution being in the titration flask and the thiocyanate in the burette.
Comparison of silver titration methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohr</td>
<td>• Simple</td>
<td>• Alkaline solutions only</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Not suitable for iodide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Requires a blank</td>
</tr>
<tr>
<td>Fajans</td>
<td>• Capability for different pH ranges and selectivity with different indicators</td>
<td>• Difficulty with dilute solutions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Should not be a high background ionic level</td>
</tr>
<tr>
<td>Volhard</td>
<td>• Capable of direct silver and indirect halide analyses</td>
<td>• Must be 1M nitric acid solution</td>
</tr>
<tr>
<td></td>
<td>• Very clear colour change</td>
<td>• Some problems with specific anions</td>
</tr>
</tbody>
</table>

Concepts
1. In most titrations it does not really matter which solution is in the burette and which is in the flask. However with Mohr’s method, it is critical that the silver is in the burette and not in the flask. Explain why.
2. Why is a blank used in Mohr’s method?
3. What indicator would be suitable to analyse the concentration of iodide in the presence of chloride?
4. How would you analyse the salt content of a sauce which contains a significant level of ethanoic acid?

Applications
1. Calculate the molarity of a silver nitrate solution, given the following standardisation data:

<table>
<thead>
<tr>
<th>Mass NaCl(g)</th>
<th>Titre (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1456</td>
<td>21.2</td>
</tr>
<tr>
<td>0.1539</td>
<td>22.7</td>
</tr>
<tr>
<td>0.1487</td>
<td>21.8</td>
</tr>
</tbody>
</table>

2. Calculate the molarity of a thiocyanate solution if 20 mL aliquots of the silver solution from Q1 were titrated to endpoint with an average of 20.7 mL of the SCN solution

Standard solutions from Q1 and Q2 are used for the following questions
3. A seawater sample is analysed for its NaCl content by diluting a 20 mL aliquot to 100 mL and titrating 25 mL aliquots of the diluted sample with an average of 23.9 mL if silver nitrate. Calculate the NaCl content in g/100 mL.
4. The soluble salt content of potato chips were analysed. Calculate the % w/w of NaCl given the following data:
5. A 2.2380g sample of a mixture of NaCl and NaI was dissolved in 200.0 mL and 25mL aliquots were titrated to endpoint, using fluorescein indicator with an average of 24.8 mL. Further 25 mL aliquots were titrated, using diiododimethylfluorescein indicator with an average of 10.3 mL. Calculate the %w/w of each salt in the mixture.

6. 50.0 mL aliquots of a bromide solution were titrated to endpoint with an average of 12.3 mL of the silver solution which has been diluted accurately by a factor of 10. Calculate the concentration of bromide in mg/L.

7. Calculate the percentage of silver in an ingot, if a 0.9023g sample was dissolved in 100 mL and 25 mL aliquots were titrated to endpoint with an average of 17.9 mL of thiocyanate titrant.

8. Calculate the concentration of salt in a soy sauce sample, which is diluted accurately by a factor of 10. 25 mL aliquots of the diluted sample are mixed with 25 mL aliquots of the silver standard, and back titrated with an average of 14.6 mL of thiocyanate.

9. A waste water sample from a gold processing plant is analysed for its cyanide content by titration with silver nitrate. 50 mL aliquots of the sample are titrated to endpoint with an average of 13.2 mL of silver nitrate, which has been diluted five times. Does this sample contravene effluent regulations which limit cyanide waste to 100 mg/L?