

Argentometric Titrations

Precipitation titrations are based on reactions that yield ionic compounds of limited solubility.

The most widely used and important precipitating reagent is silver nitrate, which is used for the determination of the halogens, the halogenlike anions, mercaptans, fatty acids, and several divalent inorganic anions.

Titrations with silver nitrate are called **argentometric titrations**.

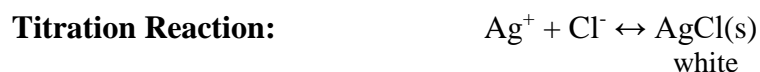
1. Mohr Method, Chromate Ion

In the Mohr method, **sodium chromate** (Na_2CrO_4) serves as the indicator for the argentometric titration of chloride, bromide, and cyanide ions.

Silver ions react with chromate to form the brick-red **silver chromate** (Ag_2CrO_4) precipitate in the equivalence-point region.

The Mohr method should be carried out at **pH 7-10**.

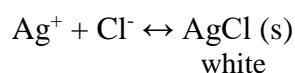
- **At low pH**; the concentration of the chromate ion in the acidic solutions is so low that it can not form a precipitate with Ag^+ at the equivalence point. Because in acidic solutions CrO_4^{2-} is converted to $\text{Cr}_2\text{O}_7^{2-}$ (Chromate ion is conjugated base of chromic acid).
- **At high pH**; the silver ions can be precipitated as Ag_2O .



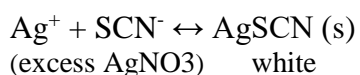
2. Volhard Method, Iron (III) Ion

In this method, **Fe (III) ion** is used as an indicator. The most important application of the Volhard method is the indirect determination of halide ions.

First, a measured excess of standard silver nitrate solution is added to the sample:

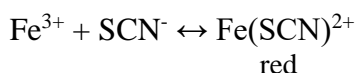


The excess silver is determined by back-titration with a standard thiocyanate solution:



Back-Titration Reaction

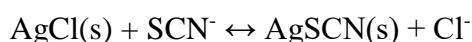
Iron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion due to the formation of Fe(SCN)²⁺.



Complexation Reaction (K: 1,05*10³)

The strongly **acidic environment** of the Volhard titration is a distinct advantage over other titrations of halide ions because such ions as carbonate, oxalate, and arsenate do not interfere. The silver salts of these ions are soluble in acidic media but only slightly soluble in neutral media.

Silver chloride is more soluble than silver thiocyanate. As a result, in chloride determinations using the Volhard method, the reaction



occurs to a significant extent near the end of the back-titration. This reaction causes the end point to fade and results in overconsumption of thiocyanate ion. The resulting low results for chloride can be overcome by filtering the silver chloride before undertaking the back-titration. Filtration is not required for other halides because they form silver salts that are less soluble than silver thiocyanate.

3. Fajans Method, Adsorption Indicator

The Fajans method uses an adsorption indicator, an organic compound that adsorbs onto or desorbs from 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 the transfer of color from the solution to the solid or vice versa.

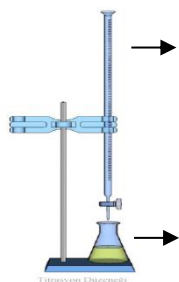
Fluorescein is a typical adsorption indicator useful for the titration of chloride ion with silver nitrate. In the aqueous solution, fluorescein is partially ionized to hydronium ions and yellowish green colored negatively charged fluoresceinate ions. The fluoresceinate ion forms a dark red silver salt.

Before the equivalence point, Cl^- is in excess, and the primary adsorbed layer is Cl^- . This repels the indicator anion, and the more loosely held secondary (counter) layer of adsorbed ions is cations, such as Na^+ .

Beyond the equivalence point, Ag^+ is in excess, and the surface of the precipitate becomes positively charged, with the primary layer being Ag^+ . This will now attract the indicator anion and adsorb it in the counterlayer.

Titration involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the few precipitation titrations that form colloidal precipitates rapidly.

Experimental Procedure:



→ 0.05 M AgNO_3 solution

- Cl^- sample + 30 mL of purified water + 3 drops of 5% CrO_4^{2-} solution → Yellow solution
- The solution is titrated until the orange color of Ag_2CrO_4 precipitate is observed in the solution.