

جامعة الانبار

كلية : الصيدلة

قسم : الكيمياء الصيدلانية

اسم المادة باللغة العربية: الكيمياء التحليلية

اسم المادة باللغة الإنكليزية: **Analytical Chemistry**

المرحلة: الاولى

التدريسي: نغم خيري كريم

عنوان المحاضرة باللغة العربية: تسحيحات الترسيب

عنوان المحاضرة باللغة الإنكليزية: **Precipitation Titration**

7.1 Introduction

Precipitation titrimetry, which is based on reactions that yield compounds of limited solubility, is one of the oldest analytical techniques, dating back to the mid-1800s. Because of the slow rate of formation of most precipitates, however, there are only a few precipitating agents that can be used in titrimetry. The most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions (SCN^- , CN^- , CNO^-), mercaptans, fatty acids, and several divalent and trivalent inorganic anions. Titrimetric methods based on silver nitrate are sometimes called **argentometric methods**.

7.2 Precipitation Titration Curves Involving Silver Ion

The most common method of determining the halide ion concentration of aqueous solutions is titration with a standard solution of silver nitrate. The reaction product is solid silver halide. A titration curve for this method usually consists of a plot pAg versus the volume of silver nitrate added. To construct titration curves, three types of calculations are required, each of which corresponds to a distinct stage in the reaction: (1) preequivalence, (2) equivalence, and (3) postequivalence.

7.3 The Effect of Concentration on Titration Curves

The effect of reagent and analyte concentrations on titration curves was shown by the two titration curves in Figure 7-1. With 0.1 M AgNO_3 (Curve A), the change in pAg in the equivalence-point region is large. With the 0.01 M reagent, the change is markedly less but still pronounced. Thus, an indicator for Ag^+ that produces a signal in the 4.0 to 6.0 pAg range should give a minimum error for the stronger solution.

For the more dilute chloride solution, the change in pAg in the equivalence-point region would be too small to be detected precisely with a visual indicator.

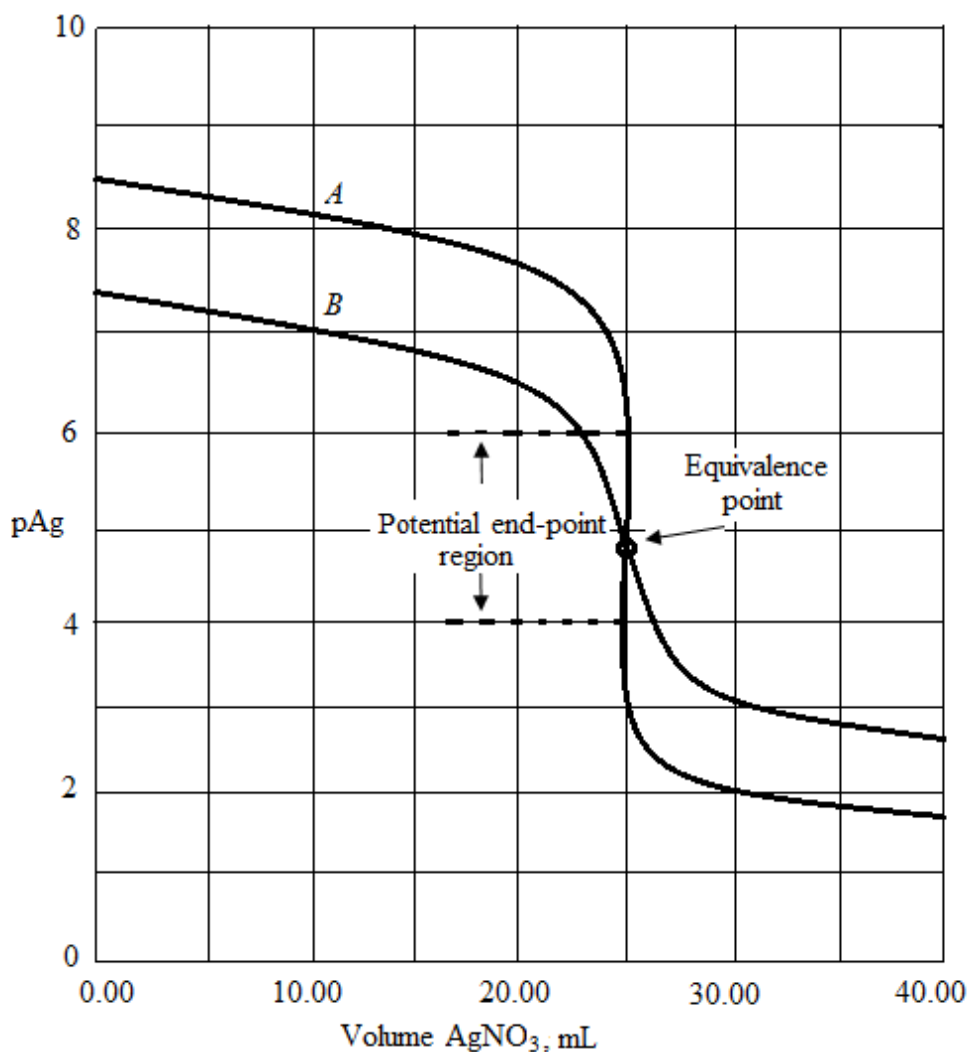


Figure 7-1 Titration Curve for A, 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃, and B, 50.00 mL of 0.00500 M NaCl with 0.0100 M AgNO₃.

7.4 Indicators for Argentometric Titrations

Three types of end points are encountered in titrations with silver nitrate: (1) chemical, (2) potentiometric, and (3) amperometric. Potentiometric end points are obtained by measuring the potential between a silver electrode and a reference electrode whose potential is

constant and independent of the added reagent. To obtain an amperometric end point, 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.

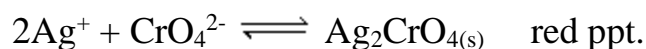
The end point produced by a chemical indicator usually consists of a color change or, occasionally, the appearance or disappearance of turbidity in the solution being titrated. The requirements for an indicator for a precipitation titration are that (1) the color change should occur over a limited range in p-function of the titrant or the analyte and (2) the color change should take place within the steep portion of the titration curve for the analyte.

7.5 Mohr's Method

Mohr's method for chloride determination depends on the titration reaction:



When all Cl^- ions react with Ag^+ ions, the first extra drop of Ag^+ will react with CrO_4^{2-} ions of the indicator forming red precipitate, and that is the end point of the reaction.



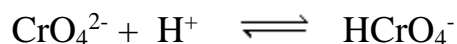
Sodium chromate can serve as an indicator for argentometric determination of chloride, bromide, and cyanide ions by reacting with silver ion to form a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region.

Silver chromate do not precipitate at the beginning, although its solubility constant is smaller than that of silver chloride, and that is because the required amount of silver ions to precipitate the chloride ions is 1.82×10^{-7} mol/L, which is much less than the amount of silver

ions required for precipitation of chromate ions (3.3×10^{-5} mol/L). Consequently, chromates precipitate after precipitation of chloride ions.

The concentration of chromate ions has an important role in determining the end point. From the calibration curve for silver nitrate with chloride we see that the equivalence point located at $pAg = 4.87$, that is, the concentration of silver ion is equal to 1.35×10^{-5} mol/L, accordingly, the chromate ions concentration required to initiate the precipitation of silver chromate is equal to 6.0×10^{-3} mol/L. In principle, this amount of chromate ions is required to start the formation of the red brick precipitate of silver chromate. This is by simply adding a slight excess of the silver solution after the equivalence point. But, since the chromate gives a bright yellow color at this concentration, which makes it impossible to see the red color of silver chromate easily, it is preferable and necessary to add a concentration less than 6.0×10^{-3} mol/L. This, of course, requires a greater concentration of the silver needed to form the red brick precipitate. This results in adding an excess amount of silver nitrate, especially in dilute solutions, so that the precipitate can be seen clearly. In both cases, there will be some error in the calibration. To overcome this difficulty, the volume taken must be corrected by titrating a volume approximately equal to the volume of the total solution at the equivalence point containing calcium carbonate and equivalent amount of the indicator then subtracting the volume of silver nitrate needed to form silver chromate precipitate, from the volume of silver reacted with the chloride.

The Mohr titration must be carried out at pH of 7 to 10 because chromate ion is the conjugate base of the weak chromic acid, react with hydrogen:





In a strong alkaline solution, the silver ions precipitate as silver oxide:



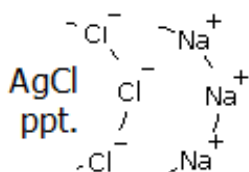
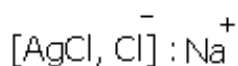
Normally, a suitable pH is achieved by saturating the analyte solution with sodium hydrogen carbonate.

7.6 Fajan's Method

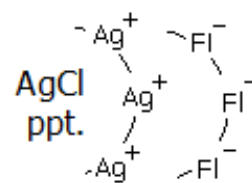
Fajan's method also called adsorption indicator, this indicator is an organic compound that tends to be adsorbed onto the surface of the solid in a precipitation titration. Ideally, the adsorption (or desorption) occurs near the equivalence point and results not only in a color change but also in a transfer of color from the solution to the solid (or the reverse).

Fluorescein is a typical adsorption indicator that is useful for the titration of chloride ion with silver nitrate. In aqueous solution, fluorescein partially dissociates into hydronium ions and negatively charged fluoresceinate ions that are yellow-green. The fluoresceinate ion forms an intensely red silver salt. Whenever this dye is used as an indicator, however, its concentration is never large enough to precipitate as silver fluoresceinate.

In the early stage of the titration of chloride ion with silver nitrate, the colloidal silver chloride particles are negatively charged because of adsorption of excess chloride ions (Figure 7.2). The dye anions are repelled from this surface by electrostatic repulsion and impart a yellow-green color to the solution.



during titration



after equivalence point

Figure 7-2 Fajan's Method for the Titration of Chloride

Beyond the equivalence point, however, the silver chloride particles strongly adsorb silver ions and thereby have 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. It is important to emphasize that the color change is an adsorption (not a precipitation) process, because the solubility product of silver fluoresceinate is never exceeded. The adsorption is reversible, the dye being desorbed on back-titration with chloride ion.

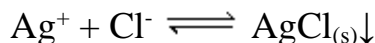
Titration involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the relatively few precipitation reactions in which a colloidal precipitate is formed rapidly.

7.7 Volhard's Method

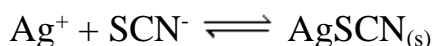
The most important application of the Volhard's method is the indirect determination of halide ions. A measured excess of standard

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

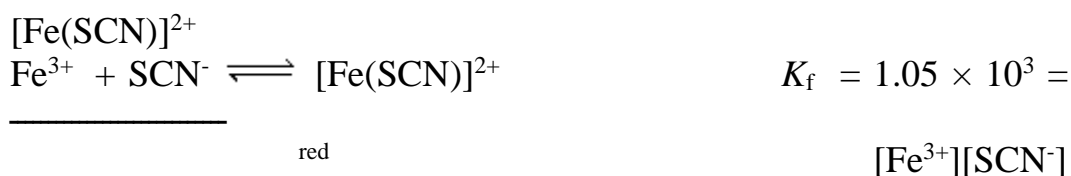
At the beginning the following reaction takes place:



Then the excess Ag^+ ions are determined by titration with standard solution of KSCN.



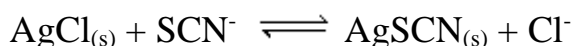
When all the Ag^+ ions are reacted SCN^- ions, the first excess drop of SCN^- will react with iron(III) ions of the indicator forming red complex indicating the end point of the reaction.



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

The strong acidic environment required for the Volhard procedure represents a distinct advantage over other titrimetric methods of halide analysis because such ions as carbonate, oxalate, and arsenate (which form slightly soluble silver salts in neutral media but not in acidic media) do not interfere.

Silver chloride is more soluble than silver thiocyanate. As a consequence, in chloride determinations by the Volhard method, the reaction:



occurs to a significant extent near the end of the back-titration of the excess silver ion. This reaction causes the end point to fade and results in an overconsumption of thiocyanate ion, which in turn 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. We can also heat the solution containing the precipitate to collect the particles together, or adding some organic solvent such as nitrobenzene or chloroform, which covers the AgCl precipitate in the bottom of conical flask and shields it from the aqueous medium which contains the excess Ag^+ .

Another application for Volhard's method is to determine AgNO_3 concentration by direct titration with thiocyanate using iron(III) ions as indicator.