PHARMACEUTICAL ANALYSIS – BP102T

UNIT: III PRECIPITATION TITRATION, COMPLEXOMETRIC TITRATION, GRAVIMETRY AND DIAZOTISATION TITRATION

CLASS:21

TOPIC: MOHRS AND VOLHARDS METHOD

MOHR'S METHOD:

- The Mohr method of determination of chlorides by titration with silver nitrate is one of the oldest titration methods still in use - it was researched and published by Karl Friedrich Mohr in 1856.

- The idea behind is very simple - chlorides are titrated with the silver nitrate solution in the presence of chromate anions.
- The appearance of the red silver chromate signals end point.

- The intense yellow color of chromate may make the detection of first signs of formation of red silver chromate precipitation difficult.
- As some excess of silver must be added before the precipitate starts to form, if the titrant concentration is below 0.1M, we may expect a significant positive error.
- To correct for this error, we can determine a blank, titrating a solution of the indicator potassium chromate with a standard silver nitrate solution.
- To make the result more realistic, we can add a small amount of chloride-free calcium carbonate to the solution to imitate the white silver precipitate.

- The solution during titration should be close to neutral. In low pH, silver chromate

solubility grows

- Due to the protonation of chromate anions, in high pH, silver starts to react with hydroxide anions,precipitating in the form of AgOH and Ag_2O.
- Both processes interfere with the determination accuracy.

  The same approach can be used for the determination of bromides. Other halides and pseudohalides, like I^- and SCN^-, behave very similarly in the solution, but their precipitate tends to adsorb chromate anions, making end-point detection difficult.

- Reaction taking place during titration is $Ag^+ + Cl^- \rightarrow AgCl(s)$

Before titration, a small amount of sodium or potassium chromate is added to the solution, making it slightly yellow in color.

During titration, as long as chlorides are present, the concentration of Ag^+ is too low for silver chromate formation.

Near equivalence point concentration of silver cations rapidly grows, allowing precipitation of intensively red silver chromate which signals end point.

To perform titration, we will need titrant - 0.1 M silver nitrate solution, indicator - potassium chromate solution, and some amount of distilled water to dilute the sample.

procedure

- Pipette an aliquot of chloride solution into a 250 mL Erlenmeyer flask.
- Dilute with distilled water to about 100 mL.
- Add 1 mL of 5% potassium chromate solution.
- Titrate with silver nitrate solution till the first color change.

According to the reaction equation $Ag^+ + Cl^- \rightarrow AgCl$

RCP

silver nitrate reacts with chloride anion on the 1:1 basis. That makes calculation especially easy -when we calculate a number of moles of $AgNO_3$ used it will be already number of moles of Cl^- titrated.

Limitations:

This method is used for solutions which are a PH range of 6 to 10. If the PH is more than 10, we get silver oxide and silver hydroxide ppt instead of silver chloride and silver bromide.

It is not carried out in the presence of a reducing agent. This method is not carried out in the presence of anions

Due to the adsorption effect, it is not used for quantitative analysis of iodides and thiocyanides. In an acidic medium, there is a need for an excess of silver, which leads to large errors

Volhard method:

It is not always possible to use the Mohr method to determine the concentration of chlorides. For example, the Mohr method requires a neutral solution, but in many cases, the solution has to be acidic to prevent precipitation of metal hydroxides (like in the presence of Fe^{3+}).
In such cases, we can use the Volhard method, which is not sensitive to low pH.

In the Volhard method, chlorides are first precipitated with excess silver nitrate, then excess silver is titrated with potassium (or sodium) thiocyanate.
To detect the end point, we use Fe3+ cations, which easily react with the thiocyanate, creating a distinct wine-red complex.

There is a problem, though. Silver thiocyanate solubility is slightly lower than solubility of silver chloride, and during titration, thiocyanate can replace chlorides in the existing

precipitate:

$$AgCl(s) + SCN^- \rightarrow AgSCN(s) + Cl^-$$

- To avoid problems, we can filtrate precipitated AgCl before titration. However, there exists a much simpler and easier procedure that gives the same result.
- Before titration, we add some small volume of a heavy organic liquid that is not miscible with water (like nitrobenzene, chloroform, or carbon tetrachloride).
- These liquids are better at wetting precipitate than water. Once the precipitate is covered with non-polar liquid, it is separated from the water and unable to dissolve.
- Precipitate solubility is not a problem during determination of I- and Br-, as both AgBr and AgI have much lower solubilities than AgSCN.

There are two reactions, as this is a back titration. First, we precipitate chlorides from the solution:

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

Then, during titration, the reaction taking place is: $Ag^+ + SCN^- \rightarrow AgSCN(s)$

In back titrations, the sample size is more difficult to calculate than during normal, direct titrations. For best accuracy, an excess of silver should be titrated with about 40-45 mL of titrant (assuming - as we usually do - that we are using a 50 mL burette).

However, that usually means we should use a relatively large initial volume of silver solution. Assuming we will start with 50 mL of pipetted silver nitrate and we will titrate excess with about 25 mL of thiocyanate solution, and finally assuming both solutions used are 0.1M, the aliquot taken for titration should contain about 0.09 g chloride anion (2.5 millimoles).

RCP

Note that silver nitrate can be added not using a single volume pipette but from the burette If the amount of chlorides is approximately known, it is possible to control the excess of silvernitrate and volume of the thiocyanate titrant.

End point detection:

The end point is detected with the use of iron (III) thiocyanate complex, which has a very distinct andstrong wine color.

To perform titration, we will need 0.1M silver nitrate solution to precipitate chlorides, titrant -0.1M potassium thiocyanate solution, nitric acid to acidify solution, ammonium ferric sulfate solution that will be used for end point detection, nitrobenzene, and some amount of distilled water to dilute sample.

Procedure:

- Pipette an aliquot of chloride solution into a 250 mL Erlenmeyer flask.
- Add 5 mL of 1+1 nitric acid.
- Dilute with distilled water to about 100 mL.
- Add 50 mL of 0.1M silver nitrate solution.
- Add 3 mL of nitrobenzene.
- Add 1 mL of iron alum solution.
- Shake the content for about 1 minute to flocculate the precipitate.
- Titrate with thiocyanate solution till the first color change.

As in every back titration, to calculate the amount of substance, we have to subtract the amount of titrated excess from the initial amount of reactant used. In the case of argentometry, calculations are easy, as all substances used react on a 1:1 basis.

RCP

First, we have to calculate a number of moles of silver nitrate initially added to the chloride sample. Assuming it was 50 mL of 0.1 M solution, it contained 5 millimoles of silver. Then,excess was titrated according to the reaction equation:

$Ag^{+} + SCN^{-} \rightarrow AgSCN(s)$

RCP