Hello students. My self Pradnyesh Satardekar, assistant professor from Ganpat Parsekar College of Education, Harmal- Goa. The title of the unit is quantitative analysis. Name of the module is, precipitation titration and choice of indicator. This is module number 10.

In this module, we will first do the introduction to precipitation titration. Next we will try to understand the shape of titration curve. Next we will see the effect of solubility product on titration curve, and finally we will see the detection of endpoint using various methods such as Mohr method, Volhard method and Fajan's method.

At the end of the module you will be able to define precipitation titration. Understand the shape of titration curve and the effect of solubility product on it. And finally, we will learn different methods for detection of endpoint using indicator.

Introduction. Students we already know that when the aqueous solution of silver ions is added to the aqueous solution of chloride, we get a precipitate of silver chloride. This type of precipitation reaction can form the basis of a titration, and this type of titration are called as precipitation titration. Precipitation titration is one of the oldest analytical technique and it dates back to mid of 1800s. Silver nitrate is one of the most commonly used precipitating reagent. The technique, the titration in which silver nitrate is used as a precipitating reagent is called as argentometric titration. In this module we will restrict ourselves only to argentometric titrations.

Now let us understand the shape of titration curve. For this, let us consider the titration of aqueous solution of chloride ion with the aqueous solution of silver nitrate to give us the precipitate of silver chloride. A titration curve is obtained when we plot pAg versus the volume of silver nitrate. Where pAg is equal to -log of concentration of silver ions. Students we see the shape of the curve. We can also note that at the equivalence point there is a rapid change in pAg. Hence, we can say that the indicator which gives a signal in the pAg range of four to six will be a good indicator which will enable us to detect the end point with minimum error.

Now let us see the effect of solubility product on titration curve. For this, let us consider the titration of aqueous solution of the X^- with the aqueous solution of silver nitrate to give the precipitate of AgX. The titration curve depends on the solubility product K_{sp} of AgX. These are the various salts of silver, and these salts are arranged in the increasing order of their solubility product. Silver iodide has the least solubility product, whereas silver bromate has the highest solubility product.

Now let us see the titration of various solution of these anions with silver nitrate. We can see that as the solubility product of the precipitate increases, the change in pAg becomes smaller and smaller. In other words, as the solubility product increases, the accurate determination of endpoints become more and more difficult. We can also see that anions, which forms a precipitate whose solubility product is greater than 10^{-10} does not yield satisfactory endpoints.

Detection of the endpoints. Endpoints can be detected in two ways. That is, either by measuring pAg with appropriate electrode and a potentiometer, or with the help of indicator. The indicator method involves Mohr method, Vollard method and Fajan's method. In this module, we will restrict ourselves only to indicator methods.

So the first method is Mohr method. In this method, a soluble chromate salt is used as an indicator. This detection is performed in slightly alkaline solution, that is in the solution having the pH of about 8. Now let us consider the determination of chloride ions by titration with silver nitrate. In this method, the first step is the addition of the chromate indicator to the solution of chloride ion, which gives a

yellow colour to the solution. The next step is titration with a solution of silver nitrate. Once all the chloride ions from the solution has been precipitated out as silver chloride, the next access of silver ions which is added to the solution, reacts with chromate to give the red precipitate of silver chromate. Hence, in this method, the end point is the solution containing the red coloured precipitate of silver chromate.

The next method is Volhard method. This method involves indirect titration for determination of anions that precipitate with silver ions. This detection is performed in acidic solution. The first step in this method is the addition of known amount of excess of silver nitrate to precipitate the anion. The next step is the determination of the access of silver ions. The excess of silver ions is determined by back titration with potassium thiocyanate solution. In this method, endpoint is detected by adding ferric alum, which forms a soluble red complex with the first excess of the titrant.

The final method is Fajan's method. This method involves adsorption indicator. Basically, adsorption indicator is an organic compound which tends to get adsorbed on the surface of the precipitate during the precipitation titration. Now let us consider determination of chloride ion by titration with silver nitrate. For this fluorescein indicator is used. Fluorescein indicator is adsorption indicator and this particular indicator in the aqueous solution partly dissociate to give H^+ ion and fluoresceinate anion, and this imparts yellow-green colour to the solution. In the early stage of titration, the precipitate of silver chloride which is obtained, is negatively charged. The reason for this is, in the early stage of titration, the concentration of the chloride ion is high. These negatively charged chloride ion get adsorbed on the surface of the precipitate. As a result, the precipitate of silver chloride becomes negatively charged. At this stage the fluoresceinate anions are electrostatically repelled by the silver chloride particles, which imparts yellow-green colour to the solution. Beyond the equivalent point, the precipitate of silver chloride becomes positively charged. The reason for this is, beyond the equivalence point, the concentration of silver ions increases. These positively charged silver ions gets adsorbed on the surface of silver chloride precipitated, and hence it becomes positively charged. Fluoresceinate anions are now attracted into the counter layer that surrounds the silver chloride particles, imparting pink colour to the solution.

To summarize, precipitation reaction can form the basis for titration. An indicator which produces signal in steep region of pAg gives minimal error. Smaller the solubility product, sharper is the endpoint. Endpoint can be detected by indicators.

These are the references.

I thank you all for the kind attention.