

Analytical Chemistry

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Objectives



At the end of this unit the student is expected to be able to :

- 1- Understand the fundamentals of precipitation titration .
- 2- Distinguish between Mohar's , Volahard's and Vajan's method ?
- 3- Realize the advantages and disadvantages of precipitation titration .
- 4- Derive the precipitation titration curve .
- 5- Evaluate the precipitation titrations .

Introduction



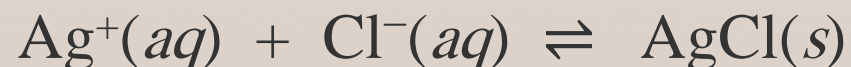
Thus far we have examined titrimetric methods based on acid–base, complexation, and redox reactions . A reaction in which the analyte and titrant form an insoluble precipitate also can serve as the basis for a titration. We call this type of titration a precipitation titration. One of the earliest precipitation titrations developed at the end of the eighteenth century was the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, was used as the titrant, forming a precipitate of CaCO_3 and CaSO_4 . The titration's end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag^+ and halide ions.

Titration Curves

A precipitation titration curve follows the change in either the analyte's or the titrant's concentration as a function of the titrant's volume. As we have done with other titrations, we will show how to calculate the titration curve .

Calculating the Titration Curve :

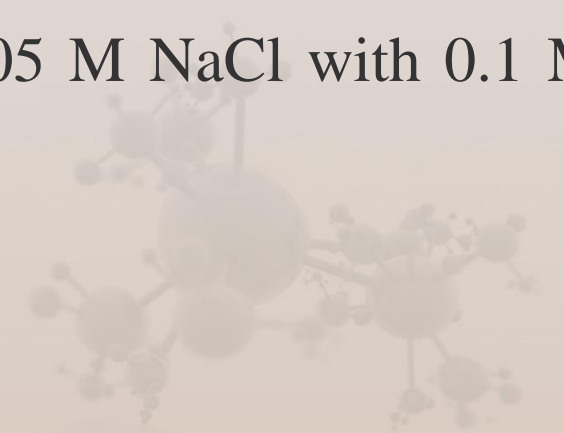
Let's calculate the titration curve for the titration of 50 mL of 0.05 M NaCl with 0.1 M AgNO₃. The reaction in this case is



Because the reaction's equilibrium constant is so large

$$K_{eq} = \frac{[\text{AgCl}]}{[\text{Ag}^+][\text{Cl}^-]} = \frac{1}{[\text{Ag}^+][\text{Cl}^-]} = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} = 5.6 \times 10^9$$

we may assume that Ag⁺ and Cl⁻ react completely.



Titration Curves

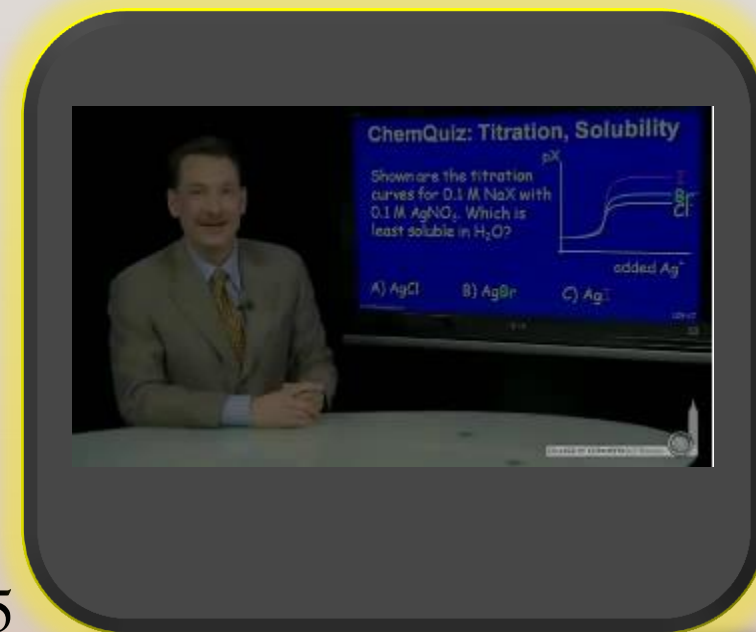
Step 1: Calculate the volume of AgNO_3 needed to reach the equivalence point : By now you are familiar with our approach to calculating a titration curve. The first task is to calculate the volume of Ag^+ needed to reach the equivalence point. The stoichiometry of the reaction requires that :

$$\begin{aligned}\text{Moles Ag}^+ &= \text{moles Cl}^- \\ M_{\text{Ag}} \times V_{\text{Ag}} &= M_{\text{Cl}} \times V_{\text{Cl}}\end{aligned}$$

Solving for the volume of Ag^+

$$V_{\text{eq.p}} = V_{\text{Ag}} = (M_{\text{Cl}} \times V_{\text{Cl}}) / M_{\text{Ag}} = (0.05 \text{ M})(50 \text{ mL}) / (0.1 \text{ M}) = 25 \text{ mL}$$

This means we need 25 mL of Ag^+ to reach the equivalence point.



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Titration Curves

Step 2: Calculate pCl before the equivalence point by determining the concentration of unreacted Cl^- : Before the equivalence point the analyt , Cl^- , is in excess. The concentration of unreacted Cl^- after adding 10 mL of Ag^+ , for example, is :

$$\begin{aligned}[\text{Cl}^-] &= (\text{initial moles } \text{Cl}^- - \text{moles } \text{Ag}^+ \text{ added}) / (\text{total volume in conical flask}) \\ &= (M_{\text{Cl}} V_{\text{Cl}} - M_{\text{Ag}} V_{\text{Ag}}) / (V_{\text{Cl}} + V_{\text{Ag}}) \\ &= (0.05 \text{ M})(50 \text{ mL}) - (0.1 \text{ M})(10 \text{ mL}) / (50 \text{ mL} + 10 \text{ mL}) = 2.5 \times 10^{-2} \text{ M}\end{aligned}$$

which corresponds to a pCl of 1.60.

Note that before the equivalent point $[\text{Ag}^+] \approx 0$ and we can calculate its real value from the K_{sp} expression ($1,8 \times 10^{-10} = (2.5 \times 10^{-2}) \times [\text{Ag}^+]$).

Step 3: Calculate pCl at the equivalence point using the K_{sp} for AgCl to calculate the concentration of Cl^- :

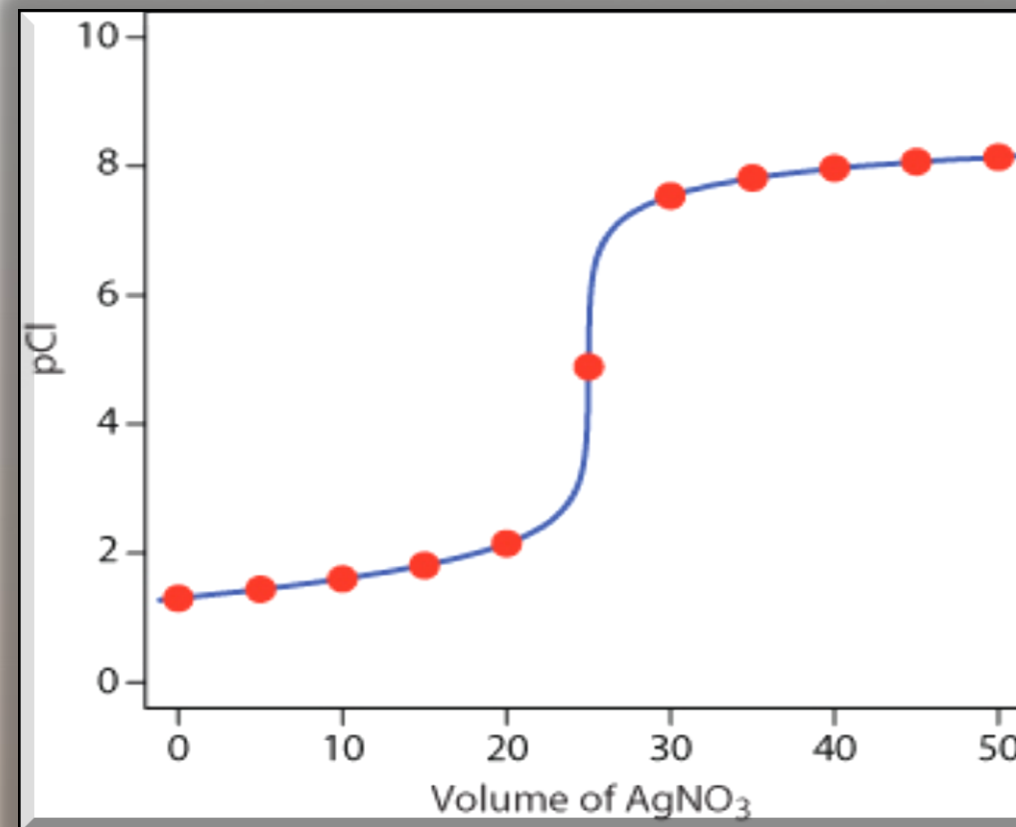
Titration Curves

At the titration's equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. To calculate the concentration of Cl^- we use the K_{sp} expression for AgCl ; thus :

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.8 \times 10^{-10}$$

Solving for x gives $[\text{Cl}^-]$ or $[\text{Ag}^+]$ as $1.3 \times 10^{-5} \text{ M}$, or a pCl of 4.89 and also $\text{pAg} = 4.89$

Step 4: Calculate pCl after the equivalence point by first calculating the concentration of excess AgNO_3 and then calculating the concentration of Cl^- using the K_{sp} for AgCl :



Titration curve for the titration of 50 mL of 0.05 M NaCl with 0.1 M AgNO_3 .

Titration Curves

After the equivalence point, the titrant is in excess. We first calculate the concentration of excess Ag^+ and then use the K_{sp} expression to calculate the concentration of Cl^- . For example, after adding 35 mL of titrant :

$$\begin{aligned}
 [\text{Ag}^+] &= (\text{moles Ag}^+ \text{ added}) - (\text{initial moles Cl}^-) / \\
 &(\text{total volume}) \\
 &= (M_{\text{Ag}} V_{\text{Ag}} - M_{\text{Cl}} V_{\text{Cl}}) / (V_{\text{Cl}} + V_{\text{ag}}) \\
 &= (0.1 \text{ M})(35 \text{ mL}) - (0.05 \text{ M})(50 \text{ mL}) / (50 \text{ mL} + \\
 &\quad 35.0 \text{ mL}) \\
 &= 1.18 \times 10^{-2} \text{ M} \text{ or } \text{pAg} = 1.93
 \end{aligned}$$

$$\begin{aligned}
 [\text{Cl}^-] &= K_{\text{sp}} / [\text{Ag}^+] = 1.8 \times 10^{-10} / 1.18 \times 10^{-2} \\
 &= 1.5 \times 10^{-8} \text{ M} \text{ or a pCl of 7.82 .}
 \end{aligned}$$

Additional results for the titration curve are shown in the previous Figure.



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Argentometric Titrations

Argentometric Titrations :

Argentometry is derived from a latin word Argentum which means silver .

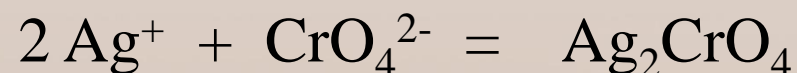
The most widely applicable precipitation titrations involve the use of silver nitrate with chlorides, bromides, iodides, and thiocyanate. Since silver is always there, precipitation titrations are referred to as Argentometric titrations. This implies that this type of titration is relatively limited.

According to end point detection method, three main procedures are widely used depending on the type of application. These are:

Argentometric Titrations (Mohr's Method)

Mohr's Method :

This method utilizes chromate as an indicator. Chromate forms a precipitate with Ag^+ but this precipitate has a greater solubility than that of AgCl , for example. Therefore, AgCl is formed first and after all Cl^- is consumed, the first drop of Ag^+ in excess will react with the chromate indicator giving a reddish precipitate.



In this method, neutral medium should be used since, in alkaline solutions $\text{pH} > 10$, silver will react with the

Argentometric Titrations (Mohr's Method)

hydroxide ions forming AgOH . In acidic solutions, chromate will be converted to HCrO_4^- and the end point is delayed . In other words silver chromate solubility grows due to the protonation of chromate anions . Therefore, the pH of solution should be kept at about 7. There is always some error in this method because a dilute chromate solution is used due to the intense color of the indicator. This will require additional amount of Ag^+ for the $\text{Ag}_2 \text{CrO}_4$ to form . This leads to a late equivalent point . To correct for this error we can determine a blank .

Argentometric Titrations (Volhard's Method)

Volhard's Method :

This is an indirect method used for determining the anions that precipitate with silver e.g Cl^- , Br^- and I^- . For example an excess amount of standard Ag^+ is added to the chloride unknown solution containing Fe^{3+} as an indicator.



The excess Ag^+ is then titrated with standard SCN^- solution



until a reddish color due to $\text{Fe}(\text{SCN})^{2+}$ complex formation is obtained which results from the reaction:

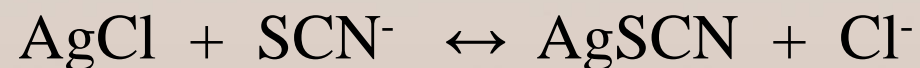


The indicator system is very sensitive and usually good results are obtained.

Argentometric Titrations (Volhard's Method)

The medium should be acidic to avoid the formation of $\text{Fe}(\text{OH})_3$.

If AgX is less soluble than AgSCN as in the case of I^- and Br^- , the excess Ag^+ can be titrated in the presence of AgX precipitate . But in the case of AgCl when SCN^- is added just after the equivalent point the following reaction will take place :



This means that , SCN^- instead of reacting with the indicator it will react with the AgCl precipitate . We have two ways to overcome this problem :

Argentometric Titrations (Volhard's Method)

The first includes addition of some organic solvent which is heavier and immiscible with water 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^+ that can be titrated with SCN^- . The second procedure involves filtration of the precipitate directly after precipitation, which protects the precipitate from coming in contact with the added SCN^- solution and titrating the excess Ag^+ in the filtrate .

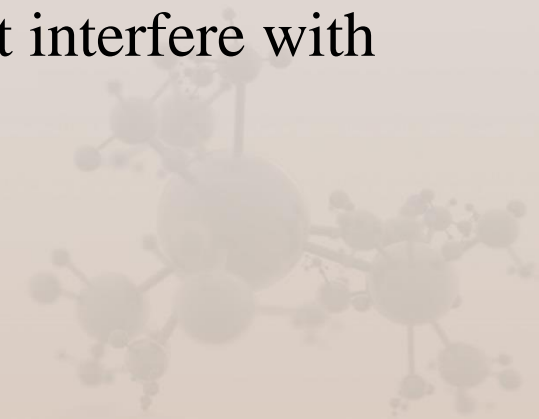
Argentometric Titrations (Volhard's Method)

Advantages of Volhard's method :

- 1- The acidic environment give advantage for halide analysis because anions such as carbonate , oxalate and arsenate that do not form precipitate with silver in acidic medium (but they do in basic medium) will not interfere with halides .
- 2- Give accurate results due to back titration .

Limitations of Volhard's method :

- 1- Can not be used in neutral or basic medium .
- 2- Time consuming .



Argentometric Titrations (Fajan's Method)

Fajan's Method :

Fluorescein and its derivatives are adsorbed to the surface of colloidal AgCl. After all chloride is used, the first drop of Ag⁺ will react with fluorescein (FI⁻) forming a reddish color.

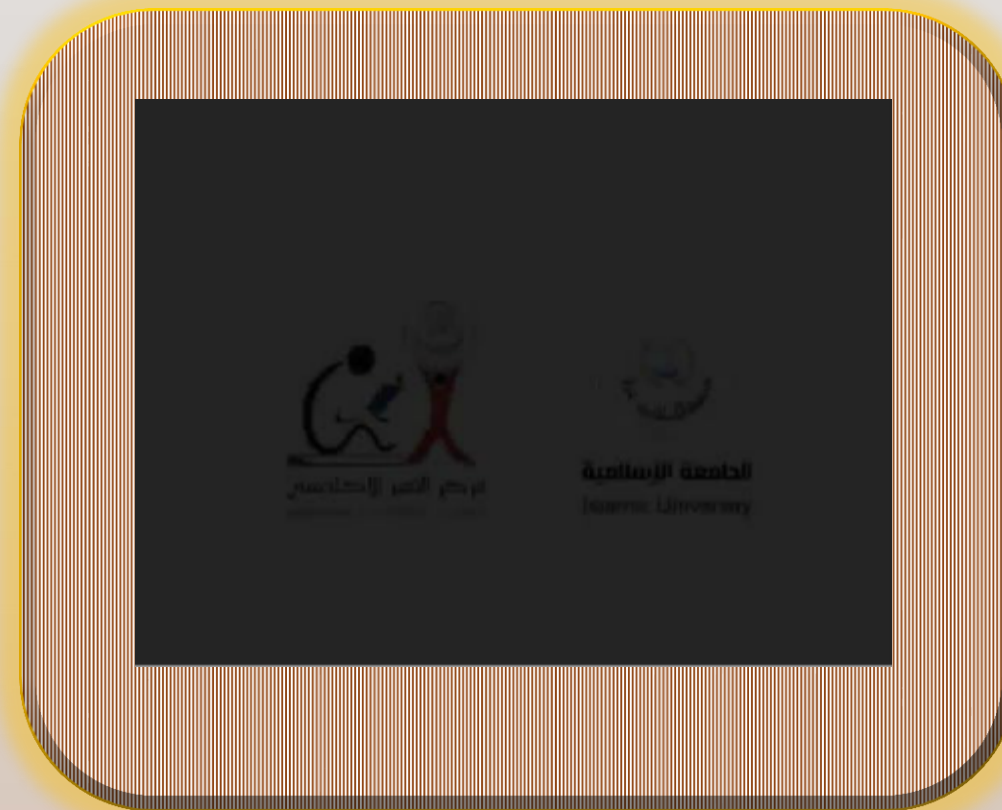


Since fluorescein and its derivatives are weak acids, the pH of the solution should be slightly alkaline to keep the indicator in the anion form but, at the same time, is not alkaline enough to convert Ag⁺ into AgOH . Fluorescein derivatives that are stronger acids than fluorescein (like eosin) can be used at acidic pH without problems. This method is simple and results obtained are reproducible.

Argentometric Titrations (Fajan's Method)

How do adsorption indicators work ?

In the Fajans method for Cl^- using Ag^+ as a titrant, for example, the anionic dye dichlorofluorescein is added to the analyt's solution. Before the end point, the precipitate of AgCl has a negative surface charge due to the adsorption of excess Cl^- . Because dichlorofluorescein also carries a negative charge, it is repelled by the precipitate and remains in solution where it has a greenish-yellow color



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Evaluation of Precipitation Titrations

After the end point, the surface of the precipitate carries a positive surface charge due to the adsorption of excess Ag^+ . Dichlorofluoroscein now adsorbs to the precipitate's surface where its color is pink. This change in the indicator's color signals the end point.

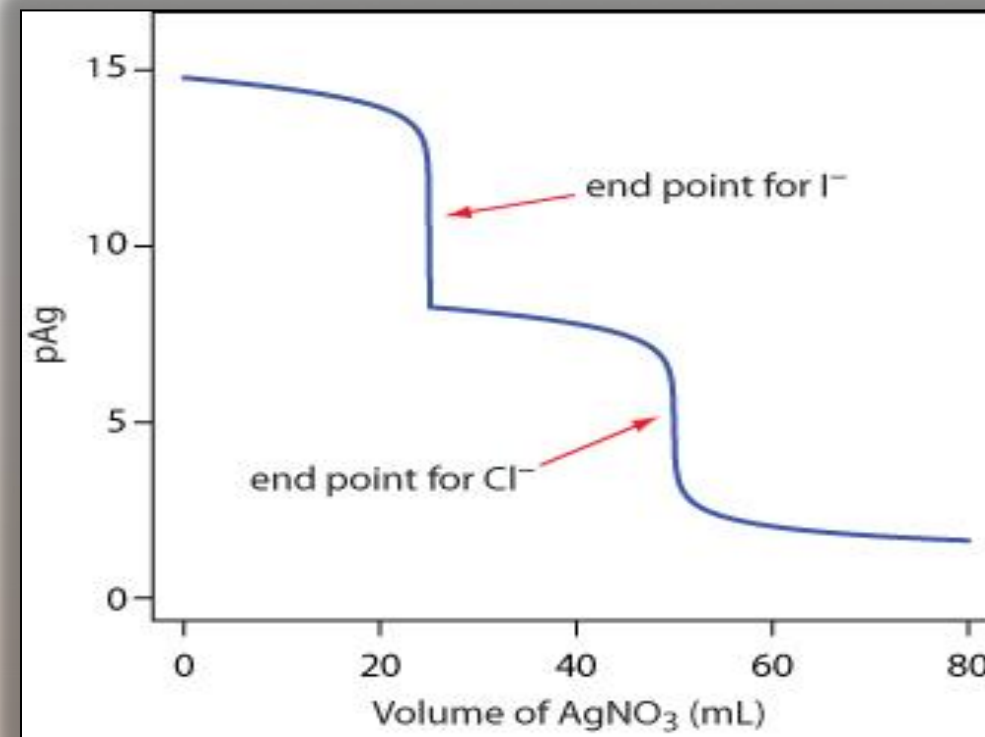
Evaluation of Precipitation Titration :

The scale of operations, accuracy, precision, sensitivity, time, and cost of a precipitation titration is similar to those described elsewhere in this course such as acid–base, complexation, and redox titrations. Precipitation titrations also can be extended to the analysis of mixtures provided that there is a significant difference in the solubility of the precipitates.

Evaluation of Precipitation Titrations

The Figure on your right shows an example of a titration curve for a mixture of I^- and Cl^- using Ag^+ as a titrant.

Although precipitation titration is rarely listed as a standard method of analysis, it may still be useful as a secondary analytical method for verifying other analytical methods



Titration curve for the titration of mixture I^- and Cl^- using Ag^+ as a titrant. Note that the end point for I^- is earlier than the end point for Cl^- because AgI is less soluble than $AgCl$.

Summary

In this unit the fundamentals of precipitation titration have been discussed and the calculations for the precipitation titration curves have been investigated. The ideas, advantages and disadvantages of each of Mohr's, Volhard's and Vajan's methods have been studied. The applications of precipitation titration are investigated. The general aspects of this unit have been clarified with relative pictures, graphs and videos.

Tutorial

Exercise 1 : A 0.32 g sample containing KCl (mw = 74.6) is dissolved in 50 mL of water and titrated to the Ag_2CrO_4 end point, requiring 16.9 mL of 0.1 M AgNO_3 . A blank titration requires 0.7 mL of titrant to reach the same end point. Report the %_{w/w} KCl in the sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 1 :

To find the moles of titrant reacting with the sample, we first need to correct for the reagent blank thus :

$$V_{\text{Ag}} = 16.9 \text{ mL} - 0.7 \text{ mL} = 16.2 \text{ mL}$$

$$(0.1 \text{ M AgNO}_3) \times (0.0162 \text{ L AgNO}_3) = 1.62 \times 10^{-3} \text{ moles of Ag}^+ = \text{moles of KCl}$$

$$\text{weight KCl} = 1.62 \times 10^{-3} \times 74.6 = 0.12 \text{ g .}$$

$$\% \text{ KCl} = (0.12 / 0.32) \times 100 = 37.5$$

Tutorial

Exercise 2 : The %_{w/w} I⁻ in a 0.6712-g sample was determined by a Volhard titration. After adding 50 mL of 0.05619 M AgNO₃ and allowing the precipitate to form, the remaining silver was back titrated with 0.05322 M KSCN, requiring 35.14 mL to reach the end point. Report the %_{w/w} I⁻ (aw = 126.9) in the sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 2 :

There are two precipitates in this analysis: AgNO_3 and I^- form a precipitate of AgI , and AgNO_3 and KSCN form a precipitate of AgSCN . Each mole of I^- consumes one mole of AgNO_3 , and each mole of KSCN consumes one mole of AgNO_3 ; thus

$$\text{moles AgNO}_3 = \text{moles I}^- + \text{moles KSCN}$$

Solving for the moles of I^- we find :

$$\text{moles I}^- = \text{moles AgNO}_3 - \text{moles KSCN}$$

$$\begin{aligned} \text{moles I}^- &= M_{\text{Ag}} \times V_{\text{Ag}} - M_{\text{KSCN}} \times V_{\text{KSCN}} \\ \text{moles I}^- &= (0.05619) \times (0.05000) - (0.05322) \times (0.03514) = 9.393 \times 10^{-4} \end{aligned}$$

$$\text{The } \%_{\text{w/w}} \text{ I}^- \text{ in the sample} = [(9.393 \times 10^{-4} \text{ mol I}^-) \times 126.9 \text{ aw I}^-] / (0.6712) \times 100 = 17.8$$

Tutorial

Exercise 3 : 400 mg of a butter was heated and some water was added . After shaking and filtration ,10 ml 0.2 M Ag^+ solution , some HNO_3 , drops of Fe^{3+} solution and some nitrobenzene were added to the Filtrate . The excess Ag^+ in the aqueous layer was titrated with 0.1 M SCN^- standard solution . If the volume of SCN^- at the equivalent point was 15 mL , calculate the percentage of NaCl (mw = 58.5) in the butter sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 3 :

$$\begin{aligned} \text{mmoles NaCl} &= \text{mmoles Cl}^- = \text{total mmoles Ag}^+ - \text{excess mmoles Ag}^+ \\ &= 10 \times 0.2 - 15 \times 0.1 = 0.5 \end{aligned}$$

$$\%_{w/w} \text{NaCl} = \frac{0.5 (\text{mmoles}) \times 58.5 (\text{mw})}{400} \times 100 = 7.3$$

Tutorial

Exercise 4 : The sulphide contents of 100 mL of a water sample was titrated with a standard solution of 0.01 M AgNO_3 according to the following reaction equation :



If the volume of AgNO_3 solution at the equivalent point was 8.5 mL , calculate the concentration (ppm) of H_2S (mw = 34) in the water sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 4 :

$$\begin{aligned} \text{mmoles } H_2S &= \text{mmoles } S^{2-} = \text{mmoles } Ag^+ \times 1/2 \\ &= 8.5 \times 0.01 \times 1/2 = 0.0425 \end{aligned}$$

$$\text{ppm } H_2S = \frac{[0.0425 (\text{mmoles}) \times 32 (\text{mw})] \text{mg}}{100 (\text{mL}) \times 10^{-3} (\text{L})} \times 100 = 1360 \text{ mg / L}$$

Tutorial

Exercise 5 : In the titration of 25 mL of 0.05 M of AgNO_3 solution with 0.02 M KSCN solution , calculate the molar concentration of Ag^+ in the conical flask solution after the following additions of titrant KSCN solution : (1) 30 mL (2) at equivalent point (3) 100 mL ? $K_{sp} (\text{AgSCN}) = 1.0 \times 10^{-12}$

Your answer :

**Our answer
next slide**

Tutorial

Answer 5 : $V_{\text{eq.p.}} = (25 \times 0.05) / 0.02 = 62.5 \text{ mL}$

(1) Before equivalent point :

$$[Ag^+] = \frac{(25 \times 0.05) - (30 \times 0.02)}{25 + 30} = 0.65 \text{ M}$$

(2) At equivalent point :

$$[Ag^+] = [SCN^-]$$

$$K_{sp} = [Ag^+][SCN^-] = [Ag^+]^2 = 1.0 \times 10^{-12}$$

$$[Ag^+] = \sqrt{1.0 \times 10^{-12}} = 1 \times 10^{-6} \text{ M}$$

(3) After equivalent point :

$$[SCN^-] = \frac{(100 \times 0.02) - (25 \times 0.05)}{100 + 25} = 6 \times 10^{-3} \text{ M}$$

$$[Ag^+] = \frac{1.0 \times 10^{-12}}{6 \times 10^{-3}} = 1.7 \times 10^{-7} \text{ M}$$

Tutorial

Exercise 6 : A 2.0 gram sample containing Cl^- (aw = 35.5 0) and ClO_4^- (mw= 99.5) was dissolved in sufficient water to give 250 mL of solution. A 50 mL aliquot required 14.0 mL of 0.09 M AgNO_3 in a Mohr's titration. A 25.00 mL aliquot was then treated with $\text{V}_2(\text{SO}_4)_3$ to reduce the ClO_4^- to Cl^- , following which titration required 40 mL of the same silver nitrate solution. Calculate the percent of Cl^- and ClO_4^- in the sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 6 :

$$\text{mmoles } \text{Cl}^- \text{ in } 50 \text{ ml} = 14 \times 0.09 = 1.26$$

$$\text{mmoles } \text{Cl}^- \text{ in } 250 \text{ ml} = \frac{1.26}{50} \times 250 = 6.3$$

$$\text{Wt. } \text{Cl}^- \text{ in sample} = 6.3 \times 35.5 = 223.65 \text{ mg} = 0.2237 \text{ g}$$

$$\% \text{Cl}^- \text{ in sample} = \frac{0.2237(\text{g})}{2.0(\text{g})} \times 100 \approx \%11.2$$

$$\text{mmoles } \text{ClO}_4^- \text{ in } 50 \text{ ml} = (40 - 14) \times 0.09 = 2.34$$

$$\text{mmoles } \text{ClO}_4^- \text{ in } 250 \text{ ml} = \frac{2.34}{50} \times 250 = 11.7$$

$$\text{Wt. } \text{ClO}_4^- \text{ in sample} = 11.7 \times 99.5 = 1164 \text{ mg} = 1.164 \text{ g}$$

$$\% \text{ClO}_4^- \text{ in sample} = \frac{1.164 \text{ g}}{2.0 \text{ g}} \times 100 = \%58.2$$

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معايير الترسيب

معايير الترسيب ٢

