Exercise no. 9

Determination of chloride in water sample using Mohr's method
Determination of chloride in water sample using Volhard's method

Mohr's method

Introduction

This method determines the chloride ion concentration of a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a white precipitate of silver chloride forms.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

The indicator used is dilute **potassium chromate** solution. When all the chloride ions have reacted, any excess silver nitrate added will react with chromate ions to form a **red-brown precipitate** of silver chromate.

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow$$

The Mohr titration should be carried out under conditions of pH 6.5 – 10.5. At higher pH silver ions may be removed by precipitation with hydroxide ions, and at low pH chromate ions may be removed by an acid-base reaction to form hydrogen chromate ions or dichromate ions, affecting the accuracy of the end point. If the solutions are acidic, the gravimetric method or Volhard's method should be used.

The Mohr titration is sensitive to the presence of both chloride and bromide ions in solution and will not be too accurate when there is a significant concentration of bromide present as well as the chloride. However, in most cases, such as seawater, the bromide concentration will be negligible. For this reason, the method can also be used to determine either the total concentration of chloride

and bromide in solution, or the concentration of bromide when the chloride concentration is known to be negligible.

Experimental procedure

Dilute the analytical sample with distilled water in a measuring flask to the mark (100 mL) and mix completely. The solution in the measuring flask should be treated as 100 mL of the water sample. **Pipette** 10 mL of the solution into the conical flask and dilute with distilled water to about 70 mL. Add 1 mL of K_2CrO_4 at a concentration of 5%. Titrate the sample with 0.05 mol/L silver nitrate solution. Because the silver chloride is a white precipitate, the chromate indicator initially gives **the cloudy solution a light lemon-yellow colour**. The endpoint of the titration is identified as the first appearance of a **red-brown colour** of silver chromate. Repeat the titration to obtain three concordant results (not differing more than 0.2 mL). Calculate the amount of chloride present in the sample using formula:

$$\mathbf{m = v \cdot c \cdot 0{,}03546 \cdot 10}$$

v – volume of $AgNO_3$ solution [mL]
c – concentration of $AgNO_3$ solution [mmol/mL]
0.03546 – mass of a millimole of Cl^- [g/mmol]

Volhard's method

Introduction

This method uses a back titration with potassium thiocyanate to determine of chloride ions in a solution. Before the titration an excess volume of a silver nitrate solution is added to the solution containing chloride ions, forming a precipitate of silver chloride. The term ‘excess‘ is used as the moles of silver nitrate added are known to exceed the moles of sodium chloride present in the sample so that all chloride ions present will react:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

The indicator Fe^{3+} (ferric ion as ferric ammonium sulfate, **$NH_4Fe(SO_4)_2$**) is then added and the solution is titrated with the potassium thiocyanate solution. The titrate remains pale yellow as the excess (unreacted) silver ions react with the thiocyanate ions to form a silver thiocyanate precipitate:

$$Ag^+ + SCN^- \rightarrow AgSCN\downarrow$$

Once all the silver ions have reacted, the slightest excess of thiocyanate reacts with Fe^{3+} to form a **dark red complex:**

$$Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$$

The concentration of chloride ions is determined by subtracting the titration findings of the moles of silver ions that reacted with the thiocyanate from the total moles of silver nitrate added to the solution.

This method is used when the pH of the solution, after the sample has been prepared, is acidic. If the pH is neutral or basic, Mohr's method or the gravimetric method should be used.

Experimental procedure

Dilute the analytical sample with distilled water in a measuring flask to the mark (100 mL) and mix completely. The solution in the measuring flask should be treated as 100 mL of the water sample. **Pipette** 10 mL of the solution into the conical flask and add 5 mL of HNO_3 (1:1) (use 10 mL measuring cylinder). Swirl to mix. Then, add (**pipette**) **15 mL** of 0.05 M $AgNO_3$ to the solution. Swirl to mix. Add 1 mL of **indicator Fe^{3+}** (10% $NH_4Fe(SO_4)_2$) to the solution. Swirl to mix **about 1 minute.** Titrate the unreacted silver ions with the 0.05 mol/L potassium thiocyanate solution (KSCN). The endpoint is the first appearance of a **dark red colour** due to the ferric thiocyanate complex. Repeat the titration to obtain three concordant results (not differing more than 0.2 mL). Calculate the amount of chloride present in the sample using formula:

$$\mathbf{m = (v \cdot c - v_1 \cdot c_1) \cdot 0.03546 \cdot 10}$$

v – volume of $AgNO_3$ solution [mL]
v_1 – volume of KSCN solution [mL]
c - concentration of $AgNO_3$ solution [mmol/mL]
c_1 - stężenie roztworu KSCN solution [mmol/mL]
0.03546 – mass of a millimole of Cl^- [g/mmol]