

# **Chapter 4**

**Removal Of Phosphate Inteference In The**

**Barium Perchlorate Titration**

**Of Sulphate**

## 4.1 Introduction

In the presence of phosphate ion, the titrimetric determination of sulphate with barium perchlorate tends to give erroneous results. This is due to the co-precipitation of barium phosphate leading to unusually high errors.

Although Schoniger<sup>145</sup> has recommended the addition of stannous chloride before titration with barium perchlorate using Thoron as indicator, this may not be always effective. Balodis et al<sup>147</sup> masked the phosphate with ferric ions in sulphate titration with barium chloride using Thoron and methylene blue as combined indicators.

Fritz and Yamamura used magnesium carbonate to remove the phosphate interference in sulphate titration with barium perchlorate, in 80% ethanol at pH 2.3 to 4. Belcher et al<sup>143</sup> used magnesium oxide for phosphate interference removal purposes. Colson<sup>144</sup> shown that silver oxide is more effective in precipitating the phosphate. Uranium acetate<sup>142</sup> was also used for phosphate removal purposes. Kristen et al<sup>27</sup> separated the phosphate using a column containing aluminium oxide and cation-exchange resin.

In this work, magnesium perchlorate was used in attempt to remove phosphate interference in titration of sulphate with barium perchlorate.

## 4.2 Experimental

### 4.2.1 Reagents and solutions

1. Sulphuric acid :  $0.0250 \text{ mol dm}^{-3}$

Prepared by dilution of concentrated volumetric solution (BDH, England)

2. Phosphoric acid:  $0.0388 \text{ mol dm}^{-3}$

Prepared by suitable dilution of concentrated phosphoric acid (BDH, England)

3. Barium perchlorate solution:  $0.025 \text{ mol dm}^{-3}$

Dissolve 16.81 g of barium perchlorate (Pro analysi, merck),  $\text{Ba}(\text{ClO}_4)_2$ , in 2 litre of distilled water and adjust pH to 3.0 with 10.0%(v/v) of perchloric acid. Standardize the solution against  $0.025 \text{ mol dm}^{-3}$  sulphuric acid with dimethylsulphanazo III as indicator.

4. Dimethylsulphanazo III indicator solution: 0.1% (w/v)

Dissolve 0.2g dimethylsulphanazo III (ICN Pharmaceuticals, New York) in  $200 \text{ cm}^3$  of distilled water.

5. Magnesium perchlorate solution:  $0.500 \text{ mol dm}^{-3}$

Dissolve 27.9g of magnesium perchlorate (Pro Analysi, Merck),  $\text{MgClO}_4$ , in  $250 \text{ cm}^3$  of distilled water.

6. Ammonium hydroxide solution solution:  $0.500 \text{ mol dm}^{-3}$

Prepared by suitable dilution of concentrated ammonia solution (Analar, Hopkin and Williams)

7. Perchloric acid : 10% (v/v)

Prepared by suitable dilution of concentrated perchloric acid (Pro Analysi, Merck).

8. Acetone; (A.R.grade, Ajax Chemicals)

9. n-Propanol: (A.R.grade, Ajax Chemicals)

## **4.2.2 Procedure**

### **4.2.2.1 Study Of Effect of pH On The Sulphate Titration.**

5.00 cm<sup>3</sup> of standard 0.025 moldm<sup>-3</sup> sulphuric acid was pipetted into a conical flask. The solution was adjusted to 50% acetone medium and then a few drops of 10% perchloric acid or 0.5 mol dm<sup>-3</sup> ammonium hydroxide solution to the required pH. Four drops of dimethylsulphonazo III indicator solution was added and the solution was titrated with standard 0.025 moldm<sup>-3</sup> barium perchlorate solution.

### **4.2.2.2 Study Of Effect Of pH On Titrimetric Determination Of Sulphate In Presence Of Phosphate**

5.00 cm<sup>3</sup> of standard 0.025 moldm<sup>-3</sup> sulphuric acid and 3.00 cm<sup>3</sup> of standard 0.0388 moldm<sup>-3</sup> phosphoric acid were pipetted into a conical flask. The solution was adjusted to 50% acetone medium and then a few drops of 10% perchloric acid or 0.5 mol dm<sup>-3</sup> ammonium hydroxide was added to the solution to adjust to the required pH. Four drops of dimethylsulphonazo III indicator solution was added and the solution was titrated with standard 0.025 moldm<sup>-3</sup> barium perchlorate solution.

### **4.2.2.3 Removal Of Phosphate Interference Using Magnesium Perchlorate Solution**

5.00 cm<sup>3</sup> of standard 0.025 mol dm<sup>-3</sup> sulphuric acid and known amount of standard 0.0388 moldm<sup>-3</sup> phosphoric acid were pipetted into a conical flask. The solution was then adjusted to pH 10-11 using 0.5 mol dm<sup>-3</sup> ammonium hydroxide solution. 10cm<sup>3</sup> of 0.500 moldm<sup>-3</sup> magnesium perchlorate solution was added to form

magnesium ammonium phosphate precipitate. The precipitate was filtered using 0.45  $\mu\text{m}$  millipore filter and washed with n-propanol, followed by distilled water. The filtrate was adjusted to 40-50% n-propanol medium. The solution was adjusted to pH 2-3 by adding a few drops of concentrated perchloric acid. Five drops of dimethylsulphonazo III indicator solution was added and the solution was titrated with standard 0.025  $\text{mol dm}^{-3}$  barium perchlorate solution.

### 4.3 Results

The effect of pH on the sulphate titration, in the absence as well as presence of phosphate, are shown Table 19 and Table 20 respectively.

**Table 19 : Effect Of pH On Titrimetric Determination Of Sulphate Using Dimethylsulphonazo III Indicator.**

PH	Volume of barium perchlorate used, $\text{cm}^3$	Relative Error*
1	5.20	0.00
2	5.19	-0.19
3	5.14	-1.15
4	5.14	-1.15
5	5.15	-0.96
6	5.17	-0.58
7	5.18	-0.38
8	5.25	0.92
9	5.32	2.31

\*Titrant value in the absence of phosphate = 5.20  $\text{cm}^3$

**Table 20: Effect Of pH In Titrimetric Determination Of Sulphate In presence Of Phosphate**

PH	Volume of barium perchlorate used, cm <sup>3</sup>	Relative Error, %*
1	5.24	0.77
2	5.40	3.85
3	5.45	4.81
4	5.50	5.77
5	5.77	10.96

\*Titrant value in the absence of phosphate = 5.20 cm<sup>3</sup>

#### 4.4 Discussion

The determination of sulphate in neutral or acidic medium was not affected by pH, as shown in Table 19. An error of approximately 1 % was observed for pH less than 7. The error increased markedly when the pH is greater than 7. This may be due to the formation of barium hydroxide as well as barium sulphate. However, this result is limited to the system containing sulphate only.

The results in Table 20 indicates that only at pH<2, the interference from phosphate is not significant. Since the indicator is barium sensitive, it responded immediately to the free barium ion that was present in the solution for pH less than 2. Whereas at the higher pH, barium ion added was used up in the formation of barium hydrogen phosphate and barium phosphate thus resulting positive error.

It was found that 4-6% positive error was produced in the determination of sulphate in the presence of phosphate, at pH 2 to 4. This suggested that titration at pH 2 to 3 can be used to assess if the removal of phosphate was successful in subsequent study.

The results for the study on the removal of phosphate using magnesium perchlorate are shown in Table 21.

**Table 21 : Removal Of Phosphate Interference In The Determination Of Sulphate, Using Magnesium Perchlorate.**

Solution with molar ration of $\text{SO}_4^{2-}$ : $\text{PO}_4^{3-}$ : $\text{Mg}(\text{ClO}_4)_2$	Volume of barium perchlorate used, $\text{cm}^3$	% Difference*
1 : 0 : 0	5.21	0.19
1 : 0 : 4	5.20	0.00
1 : 1 : 4	5.22	0.38
1 : 2 : 10	5.23	0.58
1 : 3 : 25	5.17	-0.58
1 : 5 : 40	Indistinct end-point	-

\*Compared to theoretical value of  $5.20 \text{ cm}^3$

In this study, n-propanol was chosen instead of acetone because magnesium sulphate was soluble in n-propanol. Acetone was avoid as it suppressed the solubility of magnesium sulphate.

The precipitation of phosphate as magnesium ammonium phosphate was carried out in alkaline medium ( $\sim$ pH10 to11). The used of membrane filter ( $0.45\mu\text{m}$ ) enable the precipitate to be retained. The precipitate was then washed with n-propanol. The filtrate was adjusted to 40-50% (v/v) n-propanol medium and at a pH of 2 to 3. The procedure was found to be successful and suitable for pretreatment for the sulphate titration in the presence of three times molar ration the amount of phosphate. The tolerance of the error is  $< 1\%$ .

The presence of very large excess of magnesium ions in the titration caused an indistinct end-point. The maximum tolerable concentration of magnesium ion present should not more than 25 times the concentration of the sulphate.