

Chapter 3

**Preliminary Investigations Of Potential Interfering Ions In
Titrimetric Determination of Sulphate**

3.1 Introduction

The precipitation titration of sulphate with barium perchlorate has been known to be susceptible to interference by a number of cations and anions. These interferences are due to the co-precipitation and coloured complexes formed by the certain metallic ions, especially from transition metals, with indicator.

Budensinsky⁸⁵ found that uranyl, yttrium, lanthanum, zirconium, hafnium and thorins ions interfere seriously in the sulphate determination with chlorophosphonoza III as indicator. Fritz and Yamamura¹⁴¹ have investigated the effect of foreign ions on in sulphate-barium perchlorate titration with Thoron as indicator and found that phosphate, flouride and sulphite interfere strongly and nitrate interfere at a lesser extent. Similar investigation has been carried out by Aldrich¹³⁵ with arensazo III as indicator and found similar interferences. Among the anions commonly associated with sulphate, phosphate poses the biggest problem in sulphate determination.

In this work, several potential interfering foreign ions in the sulphate titration in 50% (v/v) acetone medium with dimethylsulphonazo III as indicator was investigated. Nine cations and eight anions were studied in this work. They are lithium (as LiCl), sodium (as NaCl), potassium(as KCl), cesium (as CsCl), ammonium (as NH_4Cl), magnesium (as $\text{Mg}(\text{ClO}_4)_2$),manganese (as MnCl_2), cadmium(CdCl_2), aluminium (as AlCl_3), fluoride (as NaF), chloride (as HCl), bromide (as NaBr), iodide (as KI) , thiocyanide (as KSCN), nitrate (as HNO_3), bromate (as NaBrO_3) and phosphate (as H_3PO_4).

3.2 Procedure

5.00cm³ of standard 0.025 moldm⁻³ sulphate (as sulphuric acid) was pipetted into a conical flask. A known quantity of foreign ion under investigation was added according to foreign ion/sulphate ion molar ration of 0, 1, 2, 3, and 4. After adjusting to 50% (v/v) acetone medium, four drops of dimethylsulphonazo III indicator was added into the system. The solution was then titrated with standardised barium perchlorate solution.

3.3 Results

The results obtained for the various potential interfering cations studied are tabulated in Table 2-10 and subsequently are plotted as in Figure 1

Table 2 : Effect of Li⁺ (added as LiCl)

SO ₄ ²⁻ : Li ⁺ Ratio	Volume of Ba(ClO ₄) ₂ used, cm ³	Relative Error, %
1 : 0	5.23	0.00
1 : 1	5.26	0.57
1 : 2	5.28	0.96
1 : 3	5.29	1.15
1 : 4	5.31	1.52

Table 3 : Effect of Na^+ (added as NaCl)

$\text{SO}_4^{2-}:\text{Na}^+$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.26	0.00
1 : 1	5.21	-0.95
1 : 2	5.20	-1.14
1 : 3	5.19	-1.33
1 : 4	5.19	-1.33

Table 4 : Effect of K^+ (added as KCl)

$\text{SO}_4^{2-}:\text{K}^+$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.22	0.00
1 : 1	5.20	-0.38
1 : 2	5.17	-0.96
1 : 3	5.17	-0.96
1 : 4	5.16	-1.15

Table 5 : Effect of Cs^+ (added as CsCl)

$\text{SO}_4^{2-} : \text{Cs}^+$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.25	0.00
1 : 1	5.13	-2.29
1 : 2	5.03	-4.19
1 : 3	5.01	-4.57
1 : 4	5.00	-4.76

Table 6 : Effect of NH_4^+ (added as NH_4Cl)

$\text{SO}_4^{2-} : \text{NH}_4^+$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.21	0.00
1 : 1	5.20	-0.19
1 : 2	5.17	-0.77
1 : 3	5.15	-1.15
1 : 4	5.13	-1.54

Table 7 : Effect of Mg^{2+} [added as $\text{Mg}(\text{ClO}_4)_2$]

$\text{SO}_4^{2-} : \text{Mg}^{2+}$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.25	0.00
1 : 1	5.24	-0.19
1 : 2	5.23	-0.38
1 : 3	5.21	-0.76
1 : 4	5.20	-0.95

Table 8 : Effect of Mn^{2+} (added as MnCl_2)

$\text{SO}_4^{2-} : \text{Mn}^{2+}$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.23	0.00
1 : 1	5.26	0.57
1 : 2	5.28	0.96
1 : 3	5.32	1.72
1 : 4	5.33	1.91

Table 9 : Effect of Cd^{2+} (added as CdCl_2)

$\text{SO}_4^{2-} : \text{Cd}^{2+}$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3 .	Relative error, %
1 : 0	5.23	0.00
1 : 1	5.16	-1.34
1 : 2	5.14	-1.72
1 : 3	5.11	-2.29
1 : 4	5.09	-2.68

Table 10 : Effect of Al_3^+ (added as AlCl_3)

$\text{SO}_4^{2-} : \text{Al}_3^+$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.22	0.00
1 : 1	5.15	-0.96
1 : 2	5.08	-2.31
1 : 3	5.07	-2.50
1 : 4	5.02	-3.46

Figure 1: Percentage Error In th Titre Valur Due To The Presence Of Foreign Cations

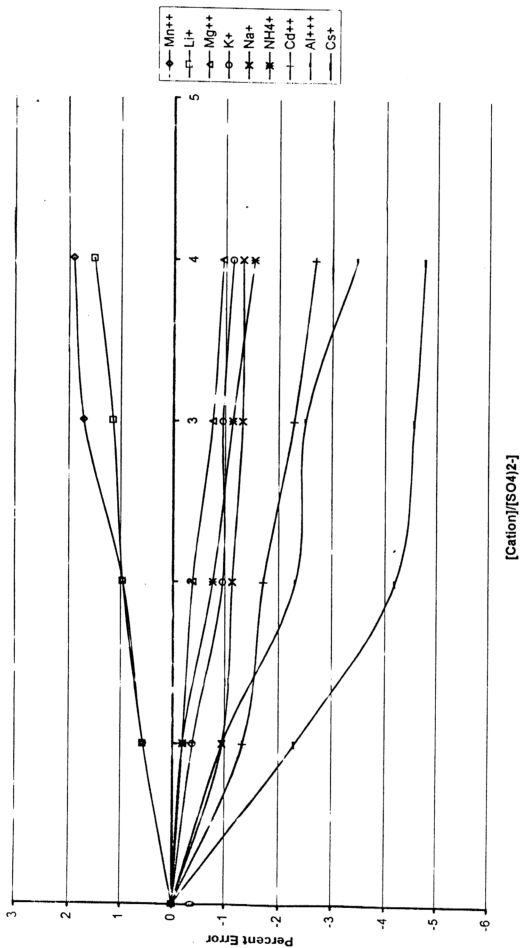


Table 11 : Effect of F^- (added as NaF)

$SO_4^{2-} : F^-$ Ratio	Volume of $Ba(ClO_4)_2$ used, cm^3	Relative error, %
1 : 0	5.25	0.00
1 : 1	5.31	1.14
1 : 2	5.34	1.71
1 : 3	5.53	5.33
1 : 4	5.68	8.20

Table 12 : Effect of Cl^- (added as HCl)

$SO_4^{2-} : Cl^-$ Ratio	Volume of $Ba(ClO_4)_2$ used, cm^3	Relative error, %
1 : 0	5.22	0.00
1 : 1	5.25	0.57
1 : 2	5.25	0.57
1 : 3	5.26	0.77
1 : 4	5.26	0.77

Table 13 : Effect of Br^- (added as NaBr)

$\text{SO}_4^{2-} : \text{Br}^-$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.23	0.00
1 : 1	5.22	-0.19
1 : 2	5.17	-0.96
1 : 3	5.16	-1.34
1 : 4	5.15	-1.53

Table 14 : Effect of I^- (added as KI)

$\text{SO}_4^{2-} : \text{I}^-$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.20	0.00
1 : 1	5.15	-0.96
1 : 2	5.11	-1.73
1 : 3	5.07	-2.50
1 : 4	5.01	-3.65

Table 15 : Effect of SCN^- (added as KSCN)

$\text{SO}_4^{2-} : \text{SCN}^-$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.23	0.00
1 : 1	5.11	-2.29
1 : 2	5.01	-4.21
1 : 3	4.98	-4.78
1 : 4	4.93	-5.74

Table 16 : Effect of NO_3^- (added as HNO_3)

$\text{SO}_4^{2-} : \text{NO}_3^-$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.22	0.00
1 : 1	5.33	2.10
1 : 2	5.36	2.68
1 : 3	5.39	3.26
1 : 4	5.42	3.83

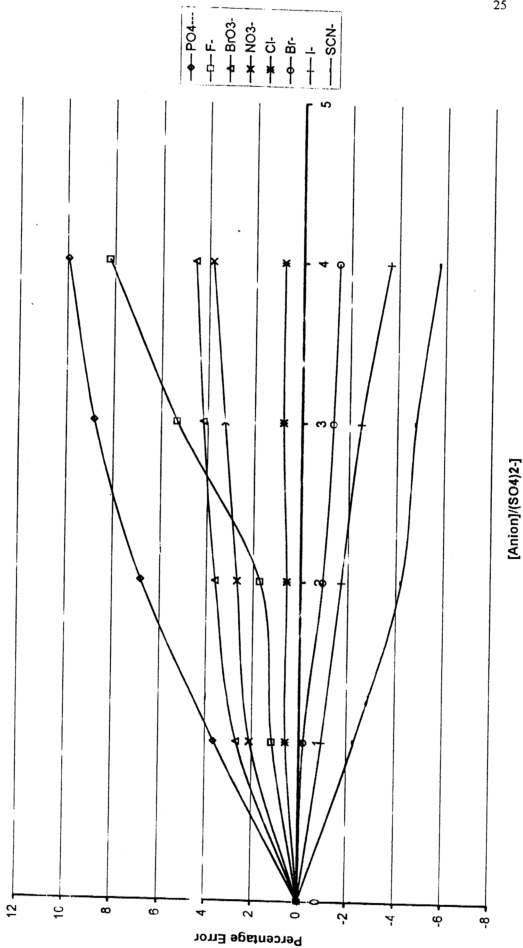
Table 17 : Effect of BrO_3^- (added as NaBrO_3)

$\text{SO}_4^{2-} : \text{BrO}_3^-$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.25	0.00
1 : 1	5.39	2.67
1 : 2	5.44	3.62
1 : 3	5.47	4.19
1 : 4	5.49	4.57

Table 18 : Effect of PO_4^{3-} (added as H_3PO_4)

$\text{SO}_4^{2-} : \text{PO}_4^{3-}$ Ratio	Volume of $\text{Ba}(\text{ClO}_4)_2$ used, cm^3	Relative error, %
1 : 0	5.23	0.00
1 : 1	5.42	3.63
1 : 2	5.59	6.80
1 : 3	5.69	8.80
1 : 4	5.75	9.94

Figure 2 : Percentage Error In The Titre Value Due To The Presence Of Foreign Anions



3.4 Discussion

3.4.1 Cation Interference

In all the cations which have been investigated, it was found that with the exception of cesium and aluminium, all the other cations investigated in this work gave an error $< 3\%$, which was within the limit of experimental error of analysis. Cesium interference is close to 5% for cation:sulphate molar ratio 4:1, whereas aluminium and cesium interference is close to 4%.

The interferences by cations can happen in two ways, namely co-precipitation and complexes formation with the indicator. Co-precipitation tends to give positive error whereas complex formation with indicator gives low value of result. Among the cations investigated, only lithium and manganese show positive errors and the other cations shown negative errors. Lithium, sodium, potassium and cesium are all in the Group I as in the periodic table. As the trend of the size of cations increases, it was learnt that the result contained larger negative errors. Being the smallest size, lithium has great tendency of co-precipitation and resulting in positive error. The tendency of forming co-precipitate is much lesser as the size of cation increases, because larger ion has lesser tendency to be included in the precipitate. For cesium, it is most likely that the size of the ion causing steric interferences and leading to pre-mature end-point being obtained.

In the presence of cadmium or aluminium in the sulphate titration, negative error was obtained. The strong positively charged aluminium ion tends to repulse the

attraction of sulphate by barium. In addition, the tendency of complexation of aluminium with indicator leads to the pre-mature end-point being detected.

3.4.2 Anion Interferences

Chloride, bromide ions show no significant interference to the system. The presence of fluoride and phosphate contributed very large positive error. This is due to the co-precipitation and insolubility or moderate solubility of the resulting precipitate. Bromate, nitrate and thiocynide caused moderate errors only.

In the presence of bromide, iodide and thiocyanide, the result were depressed. This is probably due to the size of ions which causes steric hindrance to the approach of barium ion towards sulphate ion. If the titration is carried out rather rapidly, the tendency of getting pre-mature end-point is high. It was also observed that in the presence of fluoride, chloride, iodide and nitrate at the sulphate ion / cation molar ration of 1: 2, the interferences is tolerable (<3%).

The presence of phosphate ion caused significant interference in the determination. An attempt was thus initiated to remove this interference.