

## The Effects of Several Ions on the Direct Volumetric Determination of Sulphate Ion

E. HAKOILA and PIRKKO NOPONEN

*Department of Chemistry, University of Turku, Turku, Finland*

The influence of acetate, magnesium, potassium, sodium, and ammonium ions on the direct volumetric determination of sulphate ion with a standard barium ion solution has been studied. The indicator employed was a mixture of Thorin and methylene blue. Acetate and magnesium ions have only a slight influence on the titration, but potassium, sodium, and ammonium ions reduce the volume of titrant consumed as has been found previously.<sup>1,4</sup> The resulting error is due to selective adsorption of cations on the precipitated barium sulphate. A modified method for the volumetric determination of sulphate ion in the presence of potassium, sodium, and ammonium ions is described.

Fritz and co-workers have proposed a direct volumetric method for the determination of the sulphate ion<sup>1,2</sup> in which the sample solution containing 30-40 % ethyl alcohol is titrated with a standard solution of barium chloride or barium perchlorate using Alizarin Red S or Thorin (disodium salt of *o*-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzenearsonic acid) as indicator. The authors reported the errors caused by various anions and cations. In order to eliminate the interference of cations, the solution to be analysed was deionized with a cation exchange resin. Interference by anions was eliminated by precipitating these ions<sup>2</sup> or by isolating the sulphate ion on an alumina column.<sup>3</sup> Fritz and Freeland<sup>1</sup> adjusted the pH to a suitable level with perchloric acid or magnesium acetate before the titration. Geyer<sup>4</sup> studied the influence of various salts and acetic acid on the accuracy attainable when Alizarin Red S is the indicator. Other workers who have studied the conditions and applications of the volumetric method are Wagner,<sup>5</sup> Zavarov,<sup>6</sup> Menis, Manning and Ball,<sup>7</sup> Ceausescu<sup>8</sup> and Colson.<sup>9</sup>

### EXPERIMENTAL

*Reagents.* Sulphuric acid, perchloric acid, acetic acid, barium carbonate, barium chloride, magnesium chloride, magnesium acetate, and potassium bromide were guaranteed reagents from E. Merck AG, Darmstadt. Ammonium bromide was an AnalaR reagent

and sodium bromide and magnesium bromide laboratory reagents from the British Drug Houses, Ltd. Thorin and methylene blue B were products of E. Merck AG.

*Procedure.* Various amounts of salts were added to samples containing 0.05, 0.1 or 0.5 millimole of sulphuric acid (0.5, 1.0 or 5.0 ml of 0.1 M sulphuric acid) and the resulting mixtures were diluted to 10 ml with distilled water. Five millilitres of 94.5 wt % ethyl alcohol (Grade A, State Alcohol Monopoly, Helsinki), 2 drops of a 2 % aqueous Thorin solution and 1 drop of a 0.0125 % aqueous methylene blue B solution<sup>6</sup> were added to each sample solution and the apparent pH of the solution was adjusted to 2.3–2.8 with a 0.25 M magnesium acetate solution. The solution was then titrated with a 0.05 M barium perchlorate or barium chloride solution with vigorous stirring. The titrant solutions contained about 32–33 % of ethanol by volume and were standardized against the sulphuric acid solution.

## RESULTS AND DISCUSSION

*General.* The detection of the end point of the sulphate titration becomes more difficult as the ionic strength of the sample solution increases. Values obtained when the detection of the end point was difficult for this reason are marked with asterisks in the tables. The colour change was easier to detect when light passed through the solution. All the values shown in the tables and plotted in the figures are means of six titration values.

*The effect of acetate and magnesium ions on the titration.* The effect of acetate ion on the titration is shown in Table 1 and the effects of magnesium and acetate ions together in Tables 2 and 3. The unbracketed values in the tables are millimoles of sulphuric acid and the values in parentheses the numbers of millimoles of magnesium acetate added to the solutions to adjust the apparent pH to 2.3–2.8. The data in Tables 1–3 show that acetate ion has only a slight influence on the titration when barium perchlorate and barium chloride are the titrants; only when the acetic acid content of the solution is very high (20–30 vol. per cent) does the titration result deviate appreciably from the true value. The effect of magnesium ion was studied by adding either magnesium chloride or magnesium bromide to the sample. When it is noted that chloride ion increases the titrant consumption, whereas bromide ion does not essentially alter the consumption,<sup>1</sup> it can be concluded from the data in Tables 2 and 3 that magnesium ion only slightly increases the consumption when the titrant is a barium perchlorate solution. However, magnesium ion does not seem to affect the titration when barium chloride is the titrant. These results confirm the conclusions drawn by Fritz and Freeland.<sup>1</sup>

*The effect of alkali metal ions on the titration.* Results obtained when sulphuric acid solutions containing potassium, sodium or ammonium bromide were titrated are plotted in Figs. 1, 2, and 3 or are shown in Table 4. It may be concluded that the systematic and random errors are larger when a barium chloride solution than when a barium perchlorate solution is employed as the titrant. As has been found previously,<sup>1</sup> the systematic error is greatest when potassium ion, and smallest when ammonium ion is present.

Fig. 1 shows that the systematic error increases rapidly at first when potassium bromide is added to the solution titrated (in the figures  $E_r$  is the relative error in per cent). When the titrant is a barium perchlorate solution, the relative systematic error increases with the mole ratio of potassium to sulphate ion to a limiting value ( $E_r \sim 6.5$ –7 %). When the concentration of potas-

*Table 1.* The effect of acetic acid on the titration of sulphate ion with 0.05 M barium perchlorate solution. The values are the numbers of millimoles of sulphuric acid analysed. The values in parentheses are the numbers of millimoles of magnesium acetate added to adjust the pH of the sample solutions.

Millimoles of acetic acid added	Millimoles of sulphuric acid taken		
	0.05	0.1	0.5
0	0.0500	0.100	0.500
0.05	0.0502	0.100	0.499 (0.35)
0.1	0.0502	0.100	0.498 (0.35)
0.3	0.0500	0.1001	0.497 (0.35)
0.5	0.0500	0.1002	
3.3	0.0492	0.1003	0.500 (0.35)
8.3	0.0495	0.0998 (0.025)	0.500 (0.35)
16.7	0.0493	0.1000 (0.038)	0.499 (0.38)
50	0.0490	0.0993 (0.088)	0.498 (0.42)
83 (~ 32 vol. %)	0.0483	0.0987 (0.175)	

*Table 2.* The effect of magnesium ( $MgCl_2$ ) ion and acetic acid on the titration of sulphate ion with 0.05 M barium perchlorate solution. The values are the numbers of millimoles of sulphuric acid found when titrating samples containing 0.1 millimole of sulphuric acid. The values in parentheses are the numbers of millimoles of magnesium acetate added to the sample solutions.

Millimoles of acetic acid	Millimoles of magnesium chloride			
	0.05	0.125	0.25	0.75
0	0.1001	0.1004	0.1013 * (0.038)	0.1028 * (0.05)
0.1	0.1006	0.1006	0.1021 * (0.038)	0.1042 * (0.025)
0.5	0.1008	0.1013 (0.032)	0.1026 * (0.038)	0.1041 * (0.038)
16.7	0.1008 (0.038)	0.1020 (0.062)	0.1025 (0.05)	0.1036 * (0.05)
83	0.1000 (0.175)	0.1005 (0.20)	0.1009 (0.20)	0.1015 * (0.225)

\* Detection of end point difficult.

*Table 3.* The effect of magnesium ( $MgBr_2$ ) ion and acetic acid on the titration of sulphate ion with barium salt solution. The values are the numbers of millimoles of sulphuric acid analysed in samples containing 0.1 millimole of sulphuric acid. The values in parentheses are the numbers of millimoles of magnesium acetate added to the sample solutions.

Titrant	Millimoles of acetic acid	Millimoles of magnesium bromide in the sample solution			
		0.05	0.125	0.25	0.75
$Ba(ClO_4)_2$	0	0.1007	0.1004	0.1005 (0.025)	0.1023 * (0.038)
	0.1			0.1013 (0.025)	
	0.5			0.1008 (0.025)	
	16.7			0.1008 (0.05)	
	83			0.0991 (0.20)	
$BaCl_2$	0	0.1003	0.1000	0.100 * (0.025)	0.1009 * (0.038)
	0.1	0.1005	0.1001	0.1000 (0.025)	
	0.5	0.0999	0.1002	0.1000 (0.025)	
	16.7	0.0998(0.038)	0.0998	0.0998 (0.05)	0.1004 * (0.05)
	83	0.0988(0.175)	0.0993(0.20)	0.0993 (0.20)	0.0990 * (0.225)

\* Detection of end point difficult.

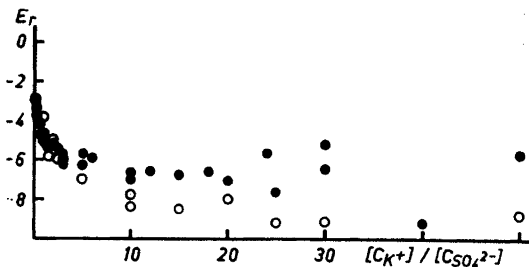


Fig. 1. Relative error in per cent as a function of the molar ratio of potassium and sulphate ions. ●  $\text{Ba}(\text{ClO}_4)_2$ ; ○  $\text{BaCl}_2$ .

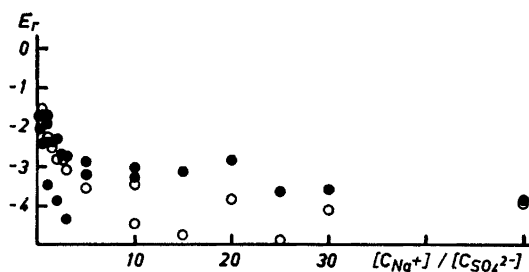


Fig. 2. Relative error in per cent as a function of the molar ratio of sodium and sulphate ions. ●  $\text{Ba}(\text{ClO}_4)_2$ ; ○  $\text{BaCl}_2$ .

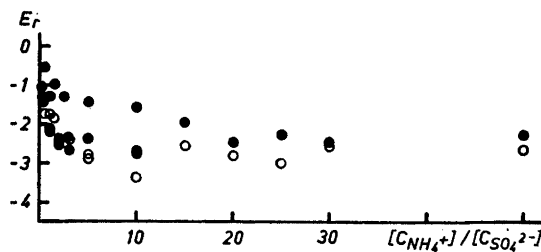


Fig. 3. Relative error in per cent as a function of the molar ratio of ammonium and sulphate ions. ●  $\text{Ba}(\text{ClO}_4)_2$ ; ○  $\text{BaCl}_2$ .

sium bromide increases further to about 2.5 millimoles/15 ml, the detection of the end point becomes more difficult and the random error increases as seen in Fig. 1. Figs. 2 and 3 show that sodium and ammonium ions have a similar effect on the sulphate titration as potassium ion. The limiting value of the relative error  $E_r$  is about 3–5 % when sodium ion and 2.5–3 % when ammonium ion is present, but varies slightly with the titrant.

When the solution titrated contains sodium bromide or ammonium bromide in addition to potassium bromide, the systematic error is practically solely

Table 4. The effect of the presence of two alkali metal ions on the titration of sulphate ion with 0.05 M barium perchlorate solution. The values are millimoles of sulphuric acid analysed in samples containing 0.1 millimole of sulphuric acid.

Added salt	Millimoles of salt added	Millimoles of potassium bromide in sample solution		
		0.1	0.25	0.5
None	—	0.0953	0.0943	0.0942
NaBr	0.1	0.0958	0.0947	0.0942
	0.25	0.0959	0.0945	0.0942
	0.5	0.0955	0.0944	0.0940
	1.0	0.0956	0.0946	
NH <sub>4</sub> Br	0.1	0.0953	0.0946	0.0939
	0.25	0.0957	0.0949	0.0939
	0.5	0.0957	0.0950	0.0948
	1.0	0.0962	0.0948	0.0945

due to the potassium ion (Table 4). The detection of the end point is more difficult when two cations are present than when potassium ion is present in a concentration equal to the sum of the concentrations of the two cations.

*Discussion.* When the effects of the individual ions are considered, attention is drawn to the limiting value of the relative error. The plots in Fig. 4 show that the relative error is in accordance with the Langmuir adsorption isotherm

$$\frac{E_r}{m} = \frac{a[M^I]}{b + [M^I]}$$

where  $E_r$  is the relative error in per cent,  $m$  the mass of precipitated barium sulphate,  $[M^I]$  the concentration of ion  $M^I$  in the titrated sample, and  $a$  and  $b$  constants. Because the indicator Thorin functions as an adsorption indicator, it is obvious that the systematic error results from the adsorption of the cation to the precipitating barium sulphate so that the precipitate is covered by a layer of cations already before the equivalence point is reached. On the basis of the conducted experiments and the results of earlier studies,<sup>1,4</sup> it may be concluded that each ion has a specific effect on the titration, which means that a selective adsorption is in question.

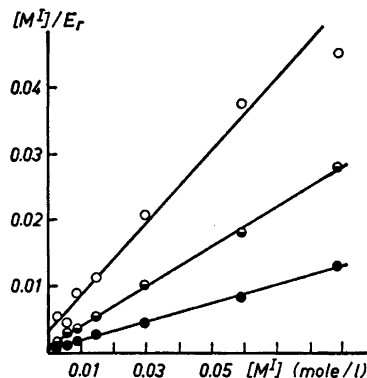


Fig. 4.  $[M^I]/E_r$  as a function of the concentration of ion  $M^I$  in the titrated sample containing 0.1 millimole of sulphate. ● KBr added; ◐ NaBr added; ○ NH<sub>4</sub>Br added.

*Sulphate titration in the presence of alkali metal ions.* Fritz and Freeland propose the removal of cations by ion exchange before sulphate ion is determined by direct titration.<sup>1</sup> The use of ion exchange may, however, be inconvenient in some cases. Geyer proposed that thorium nitrate be added to the sulphate solution when it contains alkali metal ions and Alizarin Red S as indicator to improve the colour change at the end point of the titration.<sup>4</sup> The error due to the alkali metal ion will, however, remain undiminished. On the basis of performed experiments, the following modification of the titration is proposed when alkali metal ions are present. The barium perchlorate solution used as titrant is standardized with a sulphate solution in which the concentration of potassium ion (preferably added as the bromide) is 2—2.5 times the molar concentration of the sulphate ion. Before the titration, potassium bromide is added to the sample solution until its molarity is twice the sulphate molarity. The relative titration error is then about  $\pm 1.5\%$ .

*Acknowledgements.* We express our thanks to Prof. Atte Meretoja who followed the progress of the work with interest and made valuable suggestions during the preparation of the manuscript. One of us (E. H.) has been awarded a *Government Fellowship for Younger Scientists* by the Chancellor of the University of Turku, for which he expresses his gratitude.

#### REFERENCES

1. Fritz, J. S. and Freeland, M. O. *Anal. Chem.* **26** (1954) 1593.
2. Fritz, J. S. and Yamamura, S. S. *Anal. Chem.* **27** (1955) 1461.
3. Fritz, J. S., Yamamura, S. S. and Richard, M. J. *Anal. Chem.* **29** (1957) 158.
4. Geyer, R. *Z. anal. Chem.* **146** (1955) 174.
5. Wagner, H. *Mikrochim. Acta* **1957** 19.
6. Zavarov, G. V. *Zavod. Lab.* **23** (1957) 541; *Anal. Abstr.* **4** (1957) 3640.
7. Menis, O., Manning, D. L. and Ball, R. G. *Anal. Chem.* **30** (1958) 1772.
8. Ceausescu, D. *Rev. Chim. (Bucharest)* **10** (1959) 538; *Chem. Abstr.* **57** (1962) 9211 h.
9. Colson, A. F. *Analyst* **88** (1963) 26.

Received February 12, 1965.