

The Determination of Small Quantities of Sulphate and Thiosulphate in Aqueous Solutions of Sulphur Dioxide

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Determination of low concentrations ($\sim 10^{-4}$ M) of thiosulphate and sulphate in aqueous solutions containing hydrogen sulphite/sulphur dioxide in great excess has been carried out.

A number of titrimetric methods for the analysis of mixtures of sulphite, thiosulphate and sulphate have been published.¹⁻⁵ Iguchi² has applied anion-exchange chromatography to mutual separation of the above mentioned oxy-acids of sulphur, but the method is fairly time-consuming (6-10 h). Fritz and Yamamura have published paper^{3,4} on the selective absorption of sulphate in acid solutions on a column of alumina. The sulphate is then eluted with dilute ammonium hydroxide, passed through a H^+ cation exchange resin and titrated with barium perchlorate using Thorin, *i.e.* [2-(2-hydroxy-3,6-disulpho-1-naphthylazo)]benzenearsenic acid, as indicator. The titration is known to be successful in the "apparent" pH range 2.5-4 only if a high concentration of some non-aqueous solvent is present. Sulphite interferes seriously but no distribution coefficients are given. Kurtenacker¹ describes methods based on titration without separation of the components.

The aim of the present work was to determine low concentrations, $\sim 10^{-4}$ M, of sulphate and thiosulphate in 10^{-2} M aqueous solutions of sulphur dioxide or sodium hydrogen sulphite, a problem which occurred in a study of the radiation chemistry of some oxy-acids of sulphur. The method used is a combination of the method developed by Fritz, Yamamura and Johnson^{3,4} and an iodometric titration of thiosulphate after "protection" of hydrogen sulphite by formaldehyde. The effect of having hydrogen sulphite in excess and the effect of thiosulphate on sulphate titration have, as well as the effect of sulphate on the analysis of thiosulphate, been investigated.

EXPERIMENTAL

The chemicals used were all *p.a.* quality. The concentration ranges investigated are: $[HSO_3^-] - 10^{-2}$; $2.5 \times 10^{-4} < [SO_4^{2-}] < 12.5 \times 10^{-4}$; $10^{-4} < [S_2O_3^{2-}] < 5 \times 10^{-4}$ M.

Analysis of sulphate. The alumina column, similar to the column used by Fritz and

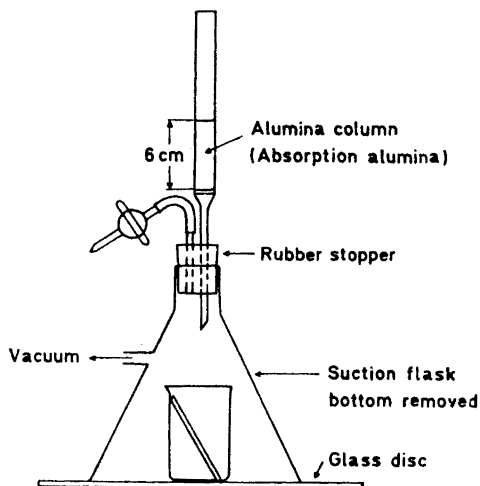


Fig. 1.

Yamamura is shown in Fig. 1. The "Acid Alumina", A G 100–200 mesh was washed with 50 ml 1 M ammonia, 4 × 5 ml 0.1 M ammonia, 50 ml water and 10 ml 1 M perchloric acid.

Perchloric acid (5 ml, 4 M) was added to 15 ml sample to obtain approximately the same ionic strength as in the column. Thus most of the hydrogen sulphite was removed as sulphur dioxide. The sample was then transferred through the column and the column washed with 10 ml of 1:20 perchloric acid and 5 × 5 ml water.

The sulphate was eluted from the column by the successive addition of 5 ml 1 M ammonia, 2 × 5 ml 0.1 M ammonia, 5 × 3 ml 0.01 M ammonia and 2 × 5 ml water. The eluate was passed through a H^+ saturated cation exchanger (Dowex 50 × 8, 20–50 mesh) and the effluent from this column diluted, with water used to wash the column, to 50 ml. A 10 ml aliquot of this final solution was titrated with 0.005 M barium chlorate in 80 % ethanol using Thorin as indicator for Ba^{2+} . To obtain a more exact value, slightly less than the required amount of barium chlorate was added quickly to another aliquot of the solution and the remaining barium chlorate added at the rate of 20–30 drops/min to a pale pink point.

The effect of thiosulphate on the titration was studied by titrating samples with increasing concentration of thiosulphate. The results obtained are tabulated in Tables 1 and 2 and the effects of thiosulphate are shown in Fig. 2. As seen from Fig. 2 and Table 2

Table 1. Determination of sulphate after separation from hydrogen sulphite-sulphur dioxide by selective absorption on alumina.

Ratio HSO_3^-/SO_4^{2-}	Ba^{2+} added ml	Ba^{2+} exp. ml	Diff. %
~ 40	0.22	0.19	- 13.6
~ 20	0.43	0.47	+ 9.3
~ 13	0.65	0.59	- 9.2
~ 13	0.82	0.88	+ 7.3
~ 10	1.09	1.11	+ 1.8

Table 2. Results of sulphate determination in presence of thiosulphate.

Ratio $\text{SO}_4^{2-}/\text{S}_2\text{O}_3^{2-}$	Ba^{2+} added ml	Ba^{2+} exp. ml	Diff. %
0	1.08	1.08	—
25.0	1.08	1.11	+ 2.7
12.5	1.08	1.14	+ 5.6
8.33	1.08	1.18	+ 9.3
6.25	1.08	1.19	+ 10.2
5.0	1.08	1.21	+ 12.0

the thiosulphate interferes seriously. The effect is, however, systematic and results can be corrected for small concentrations of $\text{S}_2\text{O}_3^{2-}$. After elution the sulphate was found to contain less than 10^{-5} M thiosulphate. This was not found to have an effect on the sulphate titration.

Analysis of thiosulphate. The method consists in complexing the hydrogen sulphite as formaldehyde—hydrogen sulphite $\text{CH}_2\text{O}\cdot\text{HSO}_3^-$, adjusting pH with acetic acid, and iodometric oxidation of thiosulphate to tetrathionate.¹ The formaldehyde—hydrogen sulphite is not affected by iodine in slightly acidic medium. The method is claimed to give good agreement for 10 ml 0.0005 M thiosulphate solution by Foerster.²

The method has in the present work been tested for 30–100 fold excess of hydrogen sulphite and the effects of 5×10^{-4} – 10^{-3} M sulphate on the method has been studied. 3 ml formaldehyde (35 % ~ 0.06 M) was added to 20 ml of the solution. The solution was allowed to stand for 5 min and then 10 ml acetic acid (10 %) was added. Starch was added and the solution was titrated with 0.01 N iodine solution to yellow-blue end point. The results are tabulated in Tables 3 and 4. As seen, the above method can be used to

Table 3. Analysis of thiosulphate in 10^{-4} M hydrogen sulphite,
 $1 \times 10^{-4} < [\text{S}_2\text{O}_3^{2-}] < 4 \times 10^{-4}$.

ml Iodine 0.00961 N ($\text{S}_2\text{O}_3^{2-}$ equiv)	ml Iodine 0.00961 N exp.	Diff. %
0.49	0.50	+ 2.0
0.75	0.755	+ 0.7
1.01	1.01	± 0.0
1.27	1.23	— 3.1
1.53	1.47	— 3.9

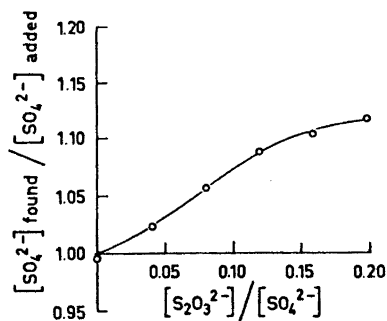


Fig. 2. The effect of thiosulphate on the sulphate analysis.

Table 4. Analysis of thiosulphate in 10^{-2} M hydrogen sulphite. The effect of sulphate on the analysis of thiosulphate, $[S_2O_3^{2-}] = 3 \times 10^{-4}$.

Ratio $[SO_4^{2-}]/[S_2O_3^{2-}]$	$(S_2O_3^{2-})$ mequiv. $\times 10^3$	Iodine mequiv. $\times 10^3$ exp.	Diff. %
No sulphate	5.81	5.81	± 0
0.83	5.81	6.17	+ 6.2
1.67	5.81	5.62	- 3.3
3.33	5.81	5.77	- 0.7
5.83	5.81	5.66	- 2.6

determine small quantities of thiosulphate ($> 10^{-6}$ mol) in aqueous solutions containing hydrogen sulphite in 50-fold excess with errors within 10 %. Sulphate in the concentration range $0 - 0.6 \times 10^{-3}$ M shows no effect within the experimental errors.

Acknowledgement. The authors express their appreciation to Professor T. Westermark, Head of this Department, for his kind interest in this work. This work was supported by *The Swedish Atomic Research Council*.

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Received March 8, 1972.