

Direct Spectrophotometric Determination of Sulphate in Aqueous Solutions of Sulphur Dioxide

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Spectrophotometric determination of sulphate (10^{-4} – 10^{-3} M) in aqueous solutions of sulphur dioxide containing hydrogen sulphite-sulphur dioxide in great excess has been studied.

The growing necessity to investigate sewage, atmospheric pollution^{1,2} and natural phenomena, *e.g.* floods, salt deposits and minerals has increased the importance of analysis of sulphuric acid and its salts. As sulphur is emitted mainly as SO_2 and H_2S the chemistry of these substances are at the moment studied extensively.¹ In the studies of radiation induced reactions in aqueous solutions of sulphur dioxide the problem of determining small concentrations (10^{-4} – 10^{-3} M) of sulphate arose.

The number of analytical methods is large^{3,4} but as several series of analyses were to be carried out our interest was focused on spectrophotometric methods. The formation of complexes between ferric ion and sulphate in 1 M perchloric acid solutions has been studied by Whitecker and Davidson.⁵ They reported the following equilibrium, dissociation constant, and maximum extinction coefficient.

$$K = [\text{Fe}^{3+}][\text{SO}_4^{2-}]/[\text{FeSO}_4^+]$$

$$K = 10^{-2} \text{ at } 28^\circ\text{C}, \epsilon(\text{FeSO}_4^+) \sim 2400 \text{ M}^{-1} \text{ cm}^{-1} \text{ at } 305 \text{ nm}$$

A very thorough spectrophotometric study has been carried out by Goguel⁶ using this complex for the determination of sulphate in natural waters. Due to interference by the formation of bisulphate ion and ferric hydroxide complex ions the acid concentration of the solution to be analysed is of great importance.⁶ Also, as the hydrated ferric ion shows an appreciable absorption at 305 nm (λ_{max} 248 nm) the analyses were carried out at larger wavelengths (326 nm).

In aqueous solution of sulphur dioxide containing $\text{SO}_{2\text{aq}}$ and HSO_3^- in great excess of SO_4^{2-} the following equilibria exist:



When the solution is acidified, the equilibria (1) and (2) are shifted to the left, *i.e.* the sulphurous species are found as $\text{SO}_{2\text{aq}}$.

Sulphur dioxide has an absorption maximum at 276 nm ($\epsilon_{\text{max}} \sim 600$) and shows an appreciable absorption even at wavelengths > 300 nm (Fig. 1). Thus sulphur dioxide, being in great excess, will interfere seriously in the sulphate analysis. The sulphur dioxide could possibly be expelled by boiling the acidified solution but this operation might cause some oxidation or disproportioning of the sulphurous species. Moreover, it is difficult to obtain a complete removal of the sulphur dioxide. Hydrogen sulphite is, however, known to form a stable addition compound with formaldehyde.^{7,8}

The aim of this work was thus to study the effect of sulphite "masking" by formaldehyde on the determination of sulphate by the ferric sulphate complex method developed by Goguel.

EXPERIMENTAL

Reagent. All chemicals used were of *p.a.* quality. The solution was prepared by dissolving the salts in double distilled water. The concentrations in the reagent were 0.1 M ferric nitrate and 1.7 M perchloric acid.

Procedure. 10 ml of the sample to be analysed was mixed with 1 ml (35 %) formaldehyde ($\text{HCHO} \sim 1.13$ M) and allowed to stand for 5 min to ensure formation of the formaldehyde-hydrogen sulphite complex. To this solution was added 1 ml of the reagent described above and the absorbance measured at 325 nm. As reference was used a mixture of 1 ml formaldehyde, 10 ml aq. dest. and 1 ml reagent.

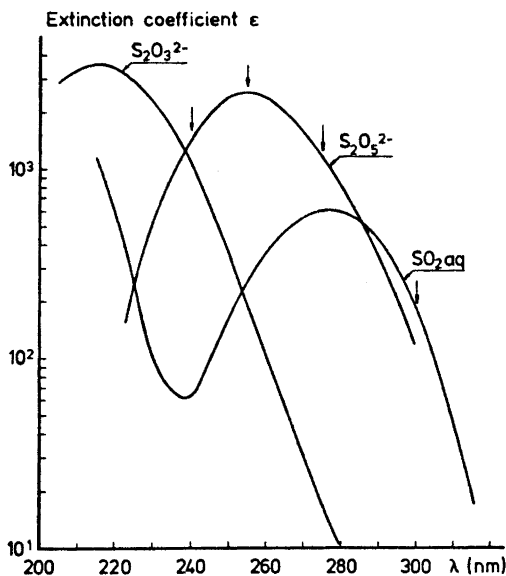
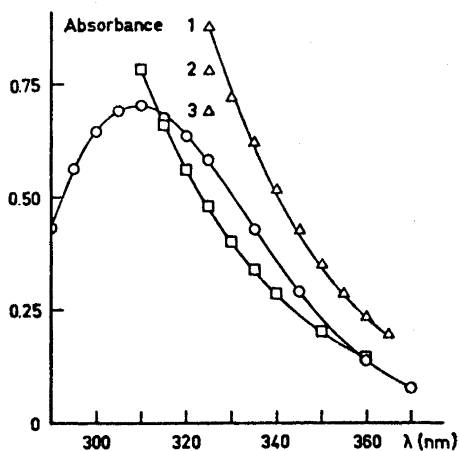


Fig. 1. Ultraviolet spectra of sulfur-oxyacids.

RESULTS AND DISCUSSION

The concentration ranges investigated are $\text{HSO}_3^- < 1.5 \times 10^{-2} \text{ M}$; $10^{-4} < \text{SO}_4^{2-} < 1.5 \times 10^{-3} \text{ M}$.

Fig. 2. $\Delta \sim 10^{-4} \text{ M SO}_4^{2-}$, $\sim 10^{-2} \text{ M SO}_2 \text{ aq}$, no formaldehyde, Pts. 1, 2, 3 show the absorbance after 0, 10, 20 minutes. \square Solution as above, but degassed. \circ Solution as above, but HSO_3^- complexed with formaldehyde before addition of reagent.



Spectra of some sulphur oxyacids are shown in Fig. 1 and the effect of sulphur dioxide on the absorption measurements is shown in Fig. 2. As seen the sulphur dioxide (in hundred-fold excess of sulphate) interferes seriously and makes the determination of sulphate in the concentration range $10^{-4} - 10^{-3} \text{ M}$ impossible. The solution is also unstable which is clearly demonstrated by the points 1, 2, and 3 in Fig. 2 showing absorbance measurement at 10 min intervals. Also shown in Fig. 2 is the spectrum obtained when the hydrogen sulphite is complexed with formaldehyde before the addition of the reagent. The spectrum is similar to the one obtained by Goguel⁶ but the absorbance obtained is higher.

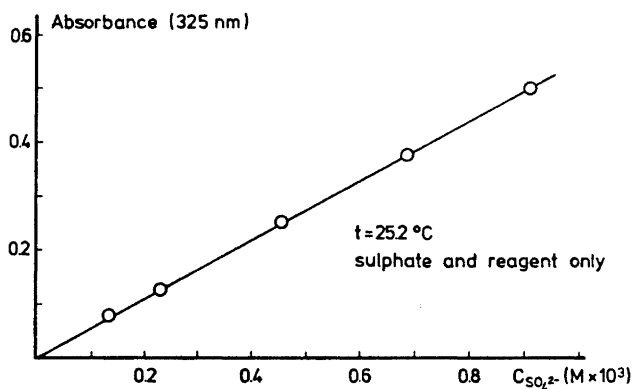


Fig. 3. Absorbance of FeSO_4^+ .

As pointed out by Goguel the acidity of the sample solution has an influence on the absorbance. This effect is, however, rather small in the acid concentration range $10^{-1} - 2 \times 10^{-1}$ M as shown in Fig. 4. A change in acid concentration from 0.13 to 0.17 M causes a 5 % change in the absorbance, as shown in Fig. 5. Also the addition of formaldehyde has an influence on the absorbance, as shown in Fig. 5. This effect is also quite small, as a four-fold increase in the formaldehyde concentration causes approximately 5 % change in the absorbance.

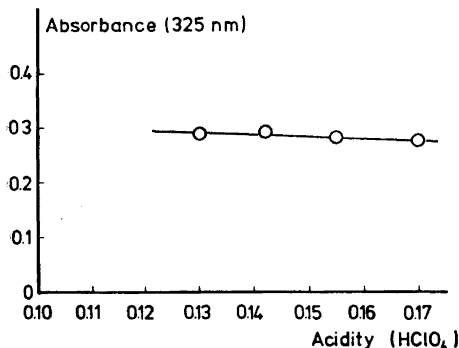


Fig. 4. Influence of acidity on absorbance at 25.2°C. FeSO_4^+ (against blank), 5×10^{-4} M SO_4^{2-} , 10^{-2} M Fe(III)nitrate.

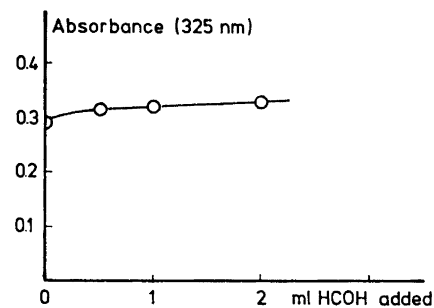


Fig. 5. Influence of formaldehyde on absorbance at 25.2°C. FeSO_4^+ (against blank), 5×10^{-4} M SO_4^{2-} , 0.142 M HClO_4 .

The influence of hydrogen sulphite concentration on the absorbance has been tested and the results are given in Fig. 6. As seen the absorbance can be assumed to be constant within the concentration range $[\text{HSO}_3^-] < 2 \times 10^{-2}$ M used in this work. The scatter is mainly due to difficulty in avoiding some oxidation of the hydrogen sulphite before addition of formaldehyde. Fig. 7 shows the linearity of FeSO_4^+ absorbance in the hydrogen sulphite-formaldehyde medium.

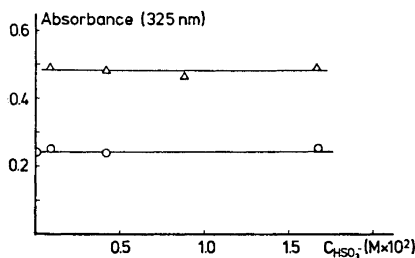


Fig. 6. Influence of HSO_3^- concentration on absorbance. O 4.17×10^{-4} M SO_4^{2-} , Δ 8.35×10^{-4} M SO_4^{2-} . 1 ml formaldehyde and 1 ml reagent were used in all experiments.

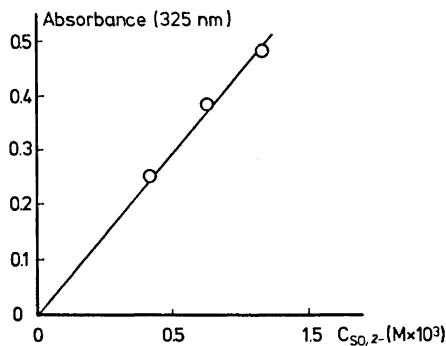


Fig. 7. Linearity test of FeSO_4^+ absorbance in hydrogen sulphite-formaldehyde medium (25.2°C). $[\text{HSO}_3^-] \sim 10^{-3}$ M, 1 ml HCHO and 1 ml reagent, sample size 10 ml.

As seen from the results above the ferric sulphate absorption method can be used to determine sulphate in the concentration range 10^{-4} – 10^{-3} M in 0 – 2×10^{-2} M hydrogen sulphite solutions or solutions of sulphur dioxide. The method can probably be applied to even higher concentrations of hydrogen sulphite or sulphur dioxide but this has not been tested. The method has, however, been tested for small concentrations of thiosulphate ($\leq 5 \times 10^{-4}$ M) and dithionate ($\leq 10^{-3}$ M) but this was not found to interfere with the analysis.

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