

CHROM. 17,499

Note

Determination of sulphite in fixers and photographic effluents by ion chromatography

MALCOLM J. McCORMICK*

Department of Applied Chemistry, Royal Melbourne Institute of Technology, GPO Box 2476V, Melbourne, Victoria 3001 (Australia)

and

LISA M. DIXON

Environment Protection Authority, 240 Victoria Parade, East Melbourne, Victoria 3002 (Australia)

(Received December 18th, 1984)

Sulphite is incorporated in photographic fixers and developers mainly to retard aerial oxidation of other components¹. Its concentration is measured for quality control purposes and in effluents it is monitored because it can deplete oxygen levels in streams and will release sulphur dioxide in contact with effluents of low pH in sewers.

Numerous procedures are available for the determination of sulphite. The method most widely used in effluent analysis is iodimetric titration², but of course this cannot be applied in the presence of thiosulphate. This problem has been overcome partly by using formaldehyde to protect sulphite from oxidation by iodine³; two titrations are needed, one with and one without the addition of formaldehyde, and the sulphite is determined by subtraction. A major problem with this procedure is that thiosulphate is always present in excess in treated effluents and spent fixers so that the ratio of thiosulphate to sulphite can be very large indeed. The subtraction of the two titration results to give a sulphite level then becomes very unreliable.

Ion chromatography⁴ has been used to determine sulphite in a number of ways, as it has been shown that the technique is unsuitable for the direct determination of sulphite because of oxidation during chromatography⁵. Holcombe *et al.*⁶ used standard solutions prepared in 10% formaldehyde while others⁵ have used sodium formaldehyde bisulphite, HOCH₂SO₃Na, as the standard material.

Lindgren *et al.*⁷ found that the addition of formaldehyde is excellent for stabilizing sulphite solutions but unfortunately they also observed that the detector response was dependent on the molar ratio of formaldehyde to sulphite and on the sulphite concentration, making calibration extremely difficult. The reason for this observation was not reported.

We have attempted to study this problem and have found that the adduct formed, being unstable in the alkaline eluents used, decomposed quickly unless further preventative measures were taken. Once stabilized, however, a very effective analytical method is obtained. The results of this study and details of the method developed are presented here.

EXPERIMENTAL

Materials

Distilled, deionised water and analytical-reagent grade chemicals were used. Formalin (M&B) contained 37–39% of formaldehyde and not less than 10% of methanol.

Standard sulphite solution (1000 mg/l) was prepared by adding 1.1872 g of sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) to about 600 ml of water containing 20 ml of formalin in a 1000-ml volumetric flask and diluting to the mark with water. Working standard solutions were prepared by diluting appropriate volumes in 2% (v/v) formalin solution.

Fixer samples were prepared by diluting 1.0 ml of fixer to 25.0 ml with water; this solution was then further diluted (1.0 ml in 50.0 ml) with 2% (v/v) formalin solution.

Instrumentation

A Dionex Model 10 ion chromatograph equipped with a 250×3 mm I.D. fast anion separator column, a 250×6 mm I.D. suppressor column and a 100- μl sample loop was used. The eluent flow-rate was 110 ml/h (23% of the maximum) and the detector was operated at 30 μmho . Either 0.003 M NaHCO_3 –0.0024 M Na_2CO_3 (eluent 1) or 0.001 M NaHCO_3 –0.2% (v/v) formalin (eluent 2) was used as the eluent.

Chromatograms were recorded using a Hewlett-Packard 3388A computing integrator and peaks were characterized by peak-height measurements.

RESULTS AND DISCUSSION

The stabilization of sulphite by formaldehyde can be demonstrated easily by comparing the ion chromatograms of sulphite solutions recorded with and without the addition of formaldehyde. This was done using a solution containing 5 mg/l of SO_3^{2-} with and without the addition of 0.005% formalin, which represents a molar excess of about 10:1. The chromatograms obtained using eluent 1 are shown in Fig. 1. Clearly the formaldehyde had stabilized the sulphite to some extent, as the amount of sulphate detected in the presence of formaldehyde had been reduced. The fact that sulphite itself was eluted, however, suggests that the adduct formed with formaldehyde was decomposed very soon after injection into the alkaline eluent.

Lindgren *et al.*⁷ studied chromatograms obtained using eluents of various pH values and found that at $\text{pH} < 10.7$ a peak was observed at a longer retention time than that of sulphite. They concluded that this peak was the stabilized adduct. However, the retention time of this component was always between those of sulphite and sulphate, and we believe that it represents an "average" retention time for a peak caused by sulphite that has oxidized to sulphate on the separator column. The size of this peak was shown⁷ to be dependent on the concentrations of both formaldehyde and sulphite, but no explanation was offered.

Increasing the concentration of formaldehyde did, in fact, reduce the size of this peak, as reported by Lindgren *et al.*⁷. However, a new peak was observed at a short retention time (Fig. 2), which increased in size as that of the sulphite peak

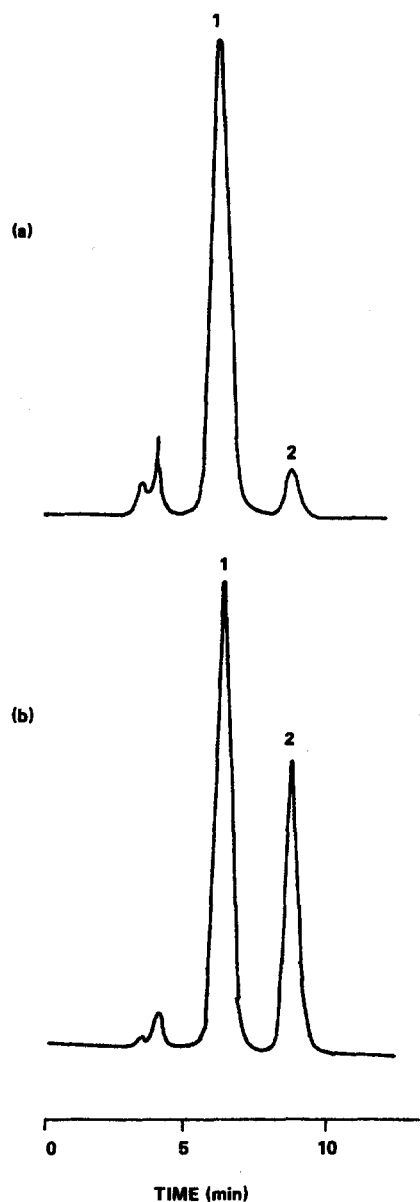


Fig. 1. Ion chromatograms of sodium metabisulphite solutions (5 mg/l of SO_3^{2-}) (a) with and (b) without the addition of 0.005% (v/v) of formalin. Eluent: 0.003 M NaHCO_3 -0.0024 M Na_2CO_3 . Peaks: 1 = sulphite; 2 = sulphate.

decreased. This is the peak which represents the stabilized anion, $\text{HOCH}_2\text{SO}_3^-$; it is understandable that increasing amounts of formaldehyde should increase the concentration of this compound at the expense of sulphite. If 1.0% (v/v) formalin or more was added, no sulphite peak was observed (Fig. 2), suggesting that at this molar ratio (2000:1) sulphite has reacted completely. The adduct was eluted early and the

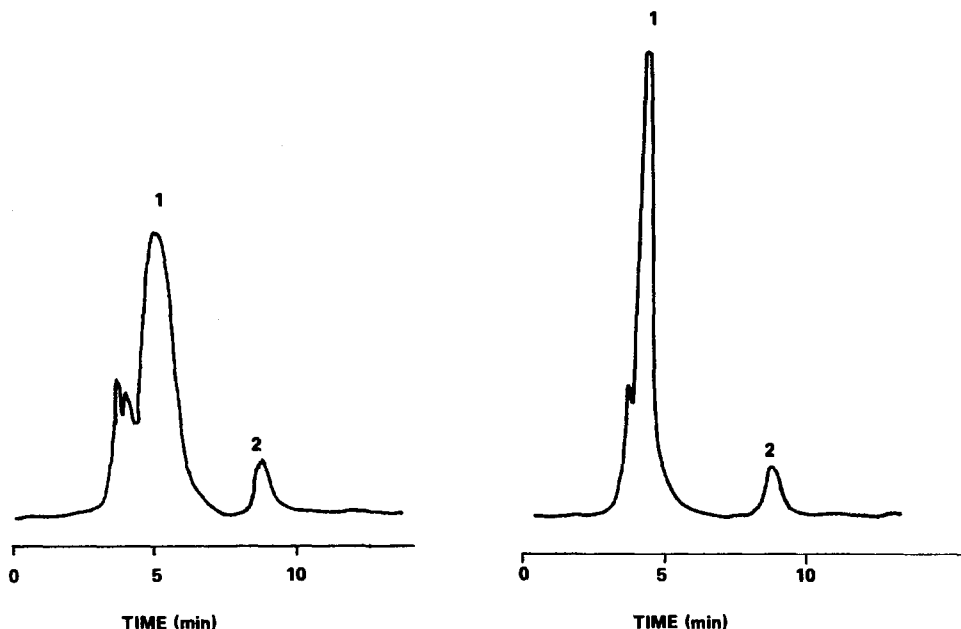


Fig. 2. Ion chromatogram of sodium metabisulphite solution (5 mg/l of SO_3^{2-}) containing 1.0% (v/v) of formalin. Eluent: 0.003 *M* NaHCO_3 -0.0024 *M* Na_2CO_3 . Peaks: 1 = $\text{HOCH}_2\text{SO}_3^-$; 2 = sulphate.

Fig. 3. Ion chromatogram of sodium metabisulphite solution (5 mg/l of SO_3^{2-}). Eluent: 0.003 *M* NaHCO_3 -0.0024 *M* Na_2CO_3 -0.2% (v/v) formalin. Peaks: 1 = $\text{HOCH}_2\text{SO}_3^-$; 2 = sulphate.

broad peak obtained suggested that decomposition was still occurring, probably owing to the high pH of the eluent. The fact that this occurred in spite of the large excess of formaldehyde was thought to be related to the fact that the adduct, being anionic, was retarded by the separator column whereas the formaldehyde was not. This was confirmed by the addition of 0.2% (v/v) formalin to the eluent, which resulted in a very sharp peak at a much shorter retention time (Fig. 3).

In order to separate this peak from the early eluting organic acids present in formalin and fixer samples, it was obvious that a more dilute eluent would be required. Successive dilutions of eluent 1 gave better but not ideal separations and so the stronger eluting sodium carbonate was omitted and dilutions of NaHCO_3 alone were used. Finally, good separations were obtained using 0.001 *M* NaHCO_3 containing 0.2% (v/v) formalin. It was found that this concentration of formaldehyde was sufficient to ensure complete stabilization of the adduct, provided that at least 1.0% (v/v) formalin was also added to the sample. This eluent, being rather weak, has two distinct advantages. First, formate, acetate, the formaldehyde bisulphite adduct and chloride are separated satisfactorily (Fig. 4). Second, the other more abundant ions, sulphate, bromide and especially thiosulphate, elute so slowly that they are not observed under these conditions and do not interfere, regardless of their concentration. Even after 30 injections of fixer solutions had been made these ions were not observed. Retained ions were easily removed from the column, however, by eluting with 0.05 *M* Na_2CO_3 for 1 h followed by a 30-minute flush with water.

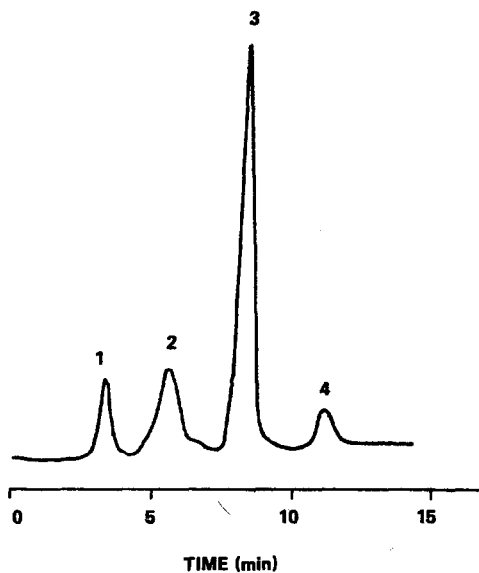


Fig. 4. Ion chromatogram of a commercial fixer diluted by a factor of 1250 with 2.0% (v/v) formalin. Eluent: 0.001 M NaHCO_3 -0.2% (v/v) formalin. Peaks: 1 = formate; 2 = acetate; 3 = $\text{HOCH}_2\text{SO}_3^-$; 4 = chloride.

A calibration graph was prepared using the procedure outlined under Experimental. A six-point plot of peak height *versus* concentration over the range 0–20 mg/l of SO_3^{2-} gave a linear graph with a regression coefficient of 0.9996. We preferred the use of sodium metabisulphite over sodium formaldehyde bisulphite as the calibration standard, even though both gave linear graphs. It was thought that the *in situ* formation of the adduct in standard solutions would more closely represent the situation found in the samples tested.

In order to test the precision, a synthetic sample was prepared that contained 8.00 mg/l of SO_3^{2-} , 200 mg/l of $\text{S}_2\text{O}_3^{2-}$ and 2.0% (v/v) of formalin. This solution was analysed six times, giving an average sulphite concentration of 8.08 mg/l with a relative standard deviation of 1.04%.

When formalin was added to undiluted fixer, a heavy white precipitate was formed. The nature of this precipitate was not investigated, but as the fixers required a two-step dilution its formation could be avoided by adding formalin after the first dilution step. This problem was not encountered with effluent samples. A commercial fixer was diluted in this way by a factor of 1250 using 2% (v/v) formalin and subjected to replicate analysis. A typical chromatogram obtained is shown in Fig. 4. In this instance the average concentration of sulphite in the fixer was found to be 8.7 g/l and the relative standard deviation was 3.7%. The extra manipulative steps involved are probably partly responsible for the slightly poorer precision in this instance, but in any event the precision of this method is still very good.

CONCLUSION

Formaldehyde has been found to be most effective in stabilizing sulphite for analytical purposes, but it has been found that it must be added to the eluent in order to achieve complete stabilization. Using this approach, a successful method has been developed for the determination of sulphite in the presence of large excesses of sulphate and/or thiosulphate.

REFERENCES

- 1 T. H. James (Editor), *The Theory of the Photographic Process*, MacMillan, New York, 3rd ed., 1969.
- 2 American Public Health Association, American Water Works Association and Water Purification Control Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 15th ed., 1980.
- 3 D. N. Fogg and N. T. Wilkinson, *J. Appl. Chem.*, 2 (1952) 357.
- 4 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 5 L. D. Hansen, B. E. Richter, D. K. Rollins, J. D. Lamb and D. J. Eatough, *Anal. Chem.*, 51 (1979) 633.
- 6 L. J. Holcombe, B. F. Jones, E. E. Ellsworth and F. B. Meserole, in J. D. Mulik and E. Sawicki (Editors), *Ion Chromatographic Analysis of Environmental Pollutants*, Ann Arbor Sci. Publ., Ann Arbor, 1979.
- 7 M. Lindgren, A. Cedergren and J. Lindberg, *Anal. Chim. Acta*, 141 (1982) 279.