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DETERMINATION OF SULPHUR OXOACIDS IN SODIUM SULPHIDE BY ISOTACHOPHORESIS

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SUMMARY

In order to determine directly $S_2O_3^{2-}$, SO_4^{2-} and SO_3^{2-} contained as impurities in sodium sulphide (Na_2S) by isotachopheresis, an investigation was made of the electrolyte system, the stability of the standard SO_3^{2-} solution and the denaturation of the Na_2S solution under different conditions of pH, temperature, concentration and dissolved oxygen content. The electrolyte system was a water-acetone (1:1) solution of $5 \cdot 10^{-3} M$ hydrochloric acid- $1 \cdot 10^{-2} M$ L-histidine as the leading electrolyte and a 0.01 M solution of sodium acetate as the terminating electrolyte, which were found to give the best results. For the solvent for the standard solution of sulphur oxoacids and the Na_2S solution, a 5% aqueous solution of glycerine prepared with water that had been degassed by boiling was found to be satisfactory. The detection limit for $S_2O_3^{2-}$, SO_4^{2-} and SO_3^{2-} in the direct analysis of an aqueous solution of Na_2S was 0.015%. The analysis time was about 15 min.

INTRODUCTION

Sodium sulphide contains various sulphur oxoacids, mainly $S_2O_3^{2-}$, SO_4^{2-} and SO_3^{2-} , which are formed during production and by subsequent oxidation. Several methods have been investigated for determining these compounds, including gravimetric¹, volumetric²⁻⁵, spectrometric⁶⁻⁸ and conductometric methods⁹⁻¹¹. In all of these methods, sulphur oxoacid ions are individually determined, and hence it is necessary to mask, or remove, coexisting ions. However, the procedures involved are difficult and time consuming.

Recently, isotachopheresis has been effectively utilized for the determination of sulphur oxoacids, the simultaneous determination¹² of $S_2O_3^{2-}$, SO_4^{2-} and SO_3^{2-} in waste water, and in the separation/determination¹³ of $S_2O_8^{2-}$ and SO_4^{2-} .

We have used isotachopheresis to determine, rapidly and simultaneously, trace amounts of $S_2O_3^{2-}$, SO_4^{2-} and SO_3^{2-} , which coexist with far greater relative amounts of S^{2-} (HS^-), and obtained satisfactory results.

EXPERIMENTAL

Sample and reagents

The sodium sulphide was commercial $Na_2S \cdot 9H_2O$.

The reagents sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), sodium sulphate (Na_2SO_4), sodium sulphite (Na_2SO_3), L-histidine · HCl, L-histidine, acetone and sodium acetate (special grade) were purchased from Wako (Osaka, Japan).

Apparatus

The apparatus was a Shimadzu IP-2A capillary-type isotachophoretic analyser equipped with a potential gradient detector. A two-stage migration tube system was used, in which a PTFE tube (1.0 mm I.D. and 50 mm long) and a fluorinated ethylene propylene tube (0.5 mm I.D. and 150 mm long) were connected in series. The migration current was set at 125 μA for 9 min and then at 50 μA until the end of the run.

Standard sample solution

A mixture of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Na_2SO_4 and Na_2SO_3 was dissolved in a 5% aqueous solution of glycerine (the water had been purified with an ion-exchange resin and degassed by boiling). The concentration obtained was $1 \cdot 10^{-3} \text{ M}$.

Sample solution

A 1% aqueous solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was prepared dissolution in water (purified with an ion-exchange resin and degassed by various methods, *i.e.*, reduced pressure, boiling and replacement of dissolved gases with nitrogen) and in $2 \cdot 10^{-3} \text{ M}$ ammonia and 5% glycerine solutions.

Isotachopheresis

Sample solutions with arbitrary volumes between 1 and 15 μl were injected directly into the analyser.

The qualitative and quantitative indices of the separated ions were expressed by means of R_E values¹⁴ (the ratio of the step height of the sample zone to that of the leading zone) and zone lengths (peak-to-peak distances).

RESULTS AND DISCUSSION

Electrolyte system

Table I shows the electrolytes used to separate $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and SO_3^{2-} by isotachopheresis. A mixture of $1 \cdot 10^{-2} \text{ M}$ hydrochloric acid, a $2 \cdot 10^{-2} \text{ M}$ aqueous solution of histidine (about pH 6.0) and acetone (30–60%) was used as the leading electrolyte. This electrolyte system provides a good separation of $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} , which are difficult to separate with an aqueous electrolyte system. An acetone concentration below 30% results in a poor separation of $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} , and a concentration above 60% results in less easy operation because of the lower electrical conductivity. In the preparation of 50% acetone solution, we found that it is better to add the acetone after the electrolytes have been dissolved.

The mobility of terminating electrolyte, CH_3COO^- , is far greater than that of S^{2-} (HS^-), the major component ion, and smaller than that of SO_3^{2-} in the electrolyte system, giving satisfactory results.

Stability of Na_2SO_3 aqueous solution

It is known that SO_3^{2-} is converted into SO_4^{2-} when the solvent contains too

TABLE I
ELECTROLYTE SYSTEM FOR SEPARATING SULPHUR OXOACIDS

| Parameter | Electrolyte | |
|---------------|------------------------|----------------------------------|
| | Leading | Terminating |
| Anion | Cl ⁻ | CH ₃ COO ⁻ |
| Concentration | 5 · 10 ⁻³ M | 1 · 10 ⁻² M |
| Counter ion | Histidine | Na ⁺ |
| Concentration | 1 · 10 ⁻² M | 1 · 10 ⁻² M |
| Solvent | Water-acetone (1:1) | Water |

much dissolved oxygen or into SO₂ if it is very acidic or alkaline. In order to obtain a stable SO₃²⁻ standard solution, a solution was prepared using water purified with an ion-exchange resin, and its change was examined with respect to time, temperature, pH and concentration.

Fig. 1 shows the time dependence of the residual yield* of SO₃²⁻ at several temperatures. The values expressed are the zone lengths relative to that just after the SO₃²⁻ had been prepared. The results show that the higher the temperature, the less the SO₃²⁻ content decreases, probably owing to the smaller amount of dissolved oxygen. It was concluded that the denaturation of SO₃²⁻ is not directly dependent on temperature.

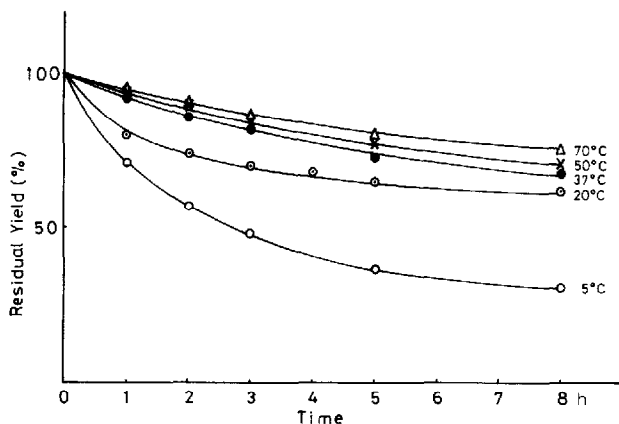


Fig. 1. Time dependence of the residual yield of SO₃²⁻ at different temperatures. A 5 · 10⁻³ M aqueous solution was prepared using water purified with an ion-exchange resin, and 5 μl of this solution were analysed.

Fig. 2 shows the time dependence of the residual yield of SO₃²⁻ at different pH values. It was found that under acidic conditions SO₃²⁻ is not converted into SO₂ but into SO₄²⁻. This is also supported by the fact that SO₃²⁻ is less converted at pH

* By residual yield is meant: the amount of the particular ion expressed relative to the amount obtained just after the preparation

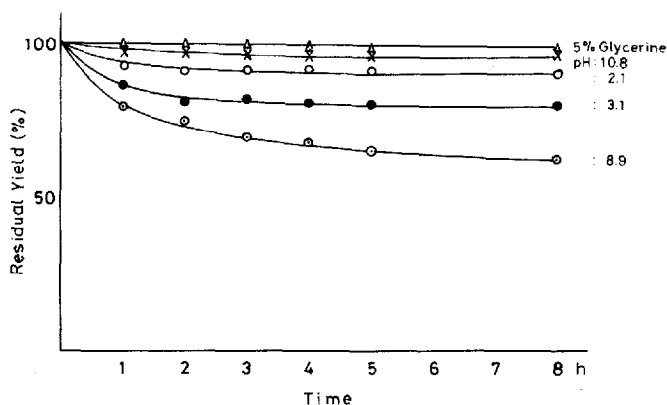


Fig. 2. Time dependence of the residual yield of SO_3^{2-} at different values. $\text{pH } 5 \cdot 10^{-3} M$ aqueous solutions were prepared using water that had been purified with an ion-exchange resin and further processed in various ways, and $5 \mu\text{l}$ of these solutions were analysed.

2.1 than at pH 3.1. The decrease is smaller in under alkaline than acidic conditions (probably owing to the lower oxygen solubility in the former). It may be concluded that the denaturation of SO_3^{2-} is not dependent on pH in the pH range 2.1–10.8.

The time dependence of the SO_3^{2-} concentration on the residual yield was examined. When the concentration was $1 M$, the yield was 98% after 8 h and 91% after 5 days. When the concentration was $1 \cdot 10^{-2} M$, the yield decreased to 80% after 8 and to 7% after 5 days. When the concentration was $1 \cdot 10^{-3} M$, the yield decreased to 46% after 8 h and to 5% after 2 days. The higher the concentration, the lower was the rate of decrease, although the absolute extent of the decrease was greater. It is desirable, therefore, that the SO_3^{2-} standard solution should have a concentration higher than $1 M$ when it is to be stored for future use.

It was concluded that the decomposition of SO_3^{2-} is dependent on the amount of dissolved oxygen. In order to decrease the amount of dissolved oxygen, 5% of glycerine is generally added to the solution at the time of preparation. We used this solution as the standard solution and obtained good results with only small changes with time, as shown in Fig. 2.

As SO_3^{2-} may be oxidized during migration, we investigated the changes in the

TABLE II
REPRODUCIBILITY OF ANALYSIS OF SULPHUR OXOACIDS

Volumes of $5 \mu\text{l}$ of the standard solution were repeatedly analysed.

| Parameter | R_E value | | | Zone length (mm)* | | |
|-----------------------|-----------------------------|--------------------|--------------------|-----------------------------|--------------------|--------------------|
| | $\text{S}_2\text{O}_3^{2-}$ | SO_3^{2-} | SO_3^{2-} | $\text{S}_2\text{O}_3^{2-}$ | SO_3^{2-} | SO_3^{2-} |
| \bar{x} ($n = 7$) | 1.330 | 1.592 | 2.105 | 17.4 | 17.1 | 11.0 |
| S.D. | 0.007 | 0.019 | 0.025 | 2.7 | 2.6 | 1.8 |
| C.V. (%) | 0.5 | 1.2 | 1.2 | 1.6 | 1.5 | 1.6 |

* Chart speed 40 mm/min.

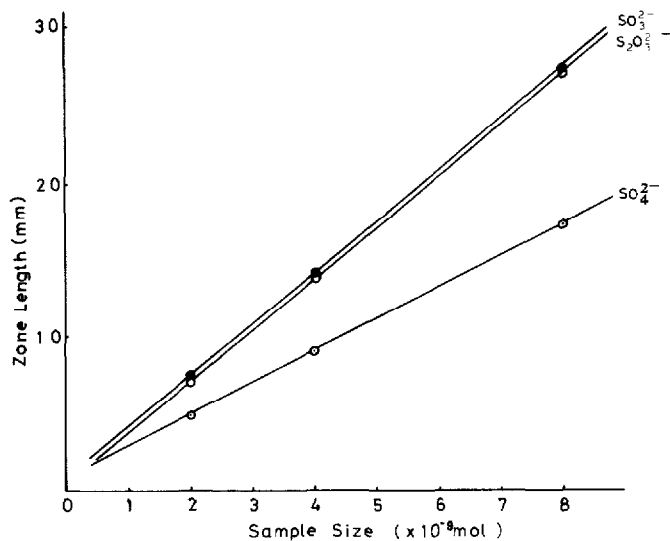


Fig. 3. Calibration graph for sulphur oxoacid ions.

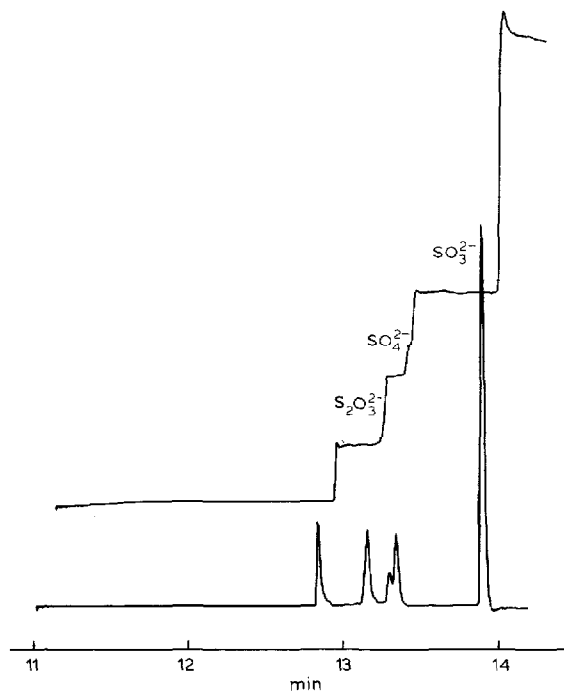


Fig. 4. Isorachopherogram of sulphur oxoacid ions in Na_2S . A 1% aqueous solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was prepared using 5% glycerine solution (prepared using water degassed by boiling), and 10 μl of this solution were analysed.

TABLE III
TIME-COURSE CHANGE OF SULPHUR OXOACIDS IN AQUEOUS SODIUM SULPHIDE SOLUTION

| <i>Treatment</i> | <i>Time (h)</i> | $S_2O_3^{2-}$ | SO_4^{2-} | SO_3^{2-} |
|-----------------------------|-----------------|---------------|-------------|-------------|
| None | 0 | 132 | 105 | 127 |
| | 1 | 155 | 137 | 150 |
| | 7 | 211 | 158 | 246 |
| Decompression | 0 | 100 | 100 | 100 |
| | 1 | 122 | 116 | 108 |
| | 7 | 148 | 132 | 115 |
| Boiling | 0 | 100 | 100 | 100 |
| | 1 | 122 | 100 | 100 |
| | 7 | 144 | 100 | 100 |
| N_2 substitution | 0 | 100 | 100 | 100 |
| | 1 | 128 | 103 | 104 |
| | 7 | 147 | 105 | 109 |
| $2 \cdot 10^{-3} M$ ammonia | 0 | 100 | 100 | 100 |
| | 1 | 122 | 100 | 115 |
| | 7 | 148 | 100 | 139 |
| 5% glycerine | 0 | 100 | 100 | 100 |
| | 1 | 100 | 100 | 100 |
| | 7 | 100 | 100 | 100 |

lengths of the zones for $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} with different migration times. Compared with a 15-min migration, a 45-min migration gave a 3.1% longer zone for SO_4^{2-} and a 4.7% shorter zone for SO_3^{2-} . The decrease and the increase in the absolute lengths of the two zones are identical, which shows that SO_3^{2-} was converted into SO_4^{2-} .

When the electrolyte was prepared with water that had been purified with an ion-exchange resin and then boiled for degassing, the oxidation of SO_3^{2-} was negligible.

TABLE IV
ANALYSIS OF SULPHUR OXOACIDS IN SODIUM SULPHIDE

| <i>Expt. No.</i> | <i>Concentration (ppm)</i> | | |
|---------------------|----------------------------|-------------|-------------|
| | $S_2O_3^{2-}$ | SO_4^{2-} | SO_3^{2-} |
| 1 | 1240 | 850 | 1520 |
| 2 | 1150 | 780 | 1440 |
| 3 | 1160 | 770 | 1450 |
| 4 | 1220 | 830 | 1540 |
| 5 | 1180 | 800 | 1450 |
| 6 | 1240 | 820 | 1540 |
| 7 | 1250 | 820 | 1510 |
| \bar{x} ($n=7$) | 1200 | 810 | 1490 |
| S.D. | 41 | 29 | 48 |
| C.V. (%) | 3.4 | 3.5 | 3.2 |

Table II shows the reproducibility of the R_E value and zone length obtained in seven repeated analyses of $5 \mu\text{l}$ of a standard solution of sulphur oxoacids.

Calibration graph

Fig. 3 shows the calibration graphs for the three sulphur oxoacid ions. Under the conditions used, the graphs are linear in for volumes of the standard solution up to $15 \mu\text{l}$ (corresponding to $1.5 \cdot 10^{-8}$ mole). The quantitative detection limit is $1 \cdot 10^{-9}$ mole. The maximum sample volume is $50 \mu\text{l}$.

Isotachopherogram

Fig. 4 shows an isochopherogram obtained in the direct analysis of a $10\text{-}\mu\text{l}$ sample solution (corresponding to 3250 ppm of Na_2S). Under the conditions used, the $\text{S}^{2-}(\text{HS}^-)$ migrates slower than the terminating ion, CH_3COO^- , and hence is not detected. If the zone of the terminating ion is continuously recorded for a long period, the $\text{S}^{2-}(\text{HS}^-)$ reaches the detector and is recorded as a step of the potential gradient signal. The maximum sample volume is $15 \mu\text{l}$. If a larger sample is injected, the electrical conductivity will be lower and bubbles are liable to be formed. The detection limit for sulphur oxoacids was 0.015% with an analysis time of about 15 min.

Denaturation of sodium sulphide

In preparation of Na_2S solution, it is necessary to prevent sulphur from being oxidized with dissolved oxygen. In order to find an electrolyte system that gives the minimum oxidation of sulphur, the yield of sulphur oxoacids was measured using water purified with an ion-exchange resin and then the degassed in various ways. It was found that $2 \cdot 10^{-3} M$ ammonia solution and a 5% solution of glycerine in boiled water are effective in preventing the oxidation of SO_3^{2-} . The results are given in Table III, which shows the zone lengths relative to those of sulphur oxoacid ions just after dissolution in water that had been degassed by boiling.

It can be concluded that boiling is the best method of degassing, but it cannot prevent the formation of $\text{S}_2\text{O}_3^{2-}$. The 5% glycerine solution can suppress the formation of sulphur oxoacids. The use of $2 \cdot 10^{-3} M$ ammonia solution is effective for the suppression of SO_4^{2-} only.

Recovery

The recovery of sulphur oxoacid ions added to a sample was determined. The sample was prepared using a standard solution of sulphur oxoacids and the zone length of each acid was measured using $10 \mu\text{l}$ of this solution. Then for a sample solution containing 5% of glycerine the zone length of each acid was measured. The yield was obtained by dividing the difference between the two zone lengths by the former. The results were 94% for $\text{S}_2\text{O}_3^{2-}$, 94% for SO_4^{2-} and 90% for SO_3^{2-} .

Table IV shows the reproducibility of analysis. The quantitative values are given as concentration (ppm) relative to Na_2S .

CONCLUSIONS

A 5% solution of glycerine in degassed water is a suitable solvent for a sample

containing sulphur oxoacids and/or sulphur that is liable to oxidation.

Trace amounts of oxoacid ions present in Na_2S can be separated by the use of a hydrochloric acid-histidine solution prepared with degassed water containing 50% of acetone as the leading electrolyte, with a terminating electrolyte containing CH_3COO^- . The quantitative detection limit in a direct analysis using the above electrolyte system was 0.015% for $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and SO_3^{2-} .

REFERENCES

- 1 W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1953.
- 2 S. Ikeda and H. Satake, *Bunseki Kagaku*, 25 (1976) 544.
- 3 S. Yamazaki, H. Ohura and I. Nakamori, *Bunseki Kagaku*, 24 (1975) 767.
- 4 B. Buděšínský, *Anal. Chem.*, 37 (1965) 1159.
- 5 J. L. Lambert, *Anal. Chim. Acta*, 54 (1970) 530.
- 6 B. H. Sörbo, *Biochim. Biophys. Acta*, 23 (1957) 412.
- 7 R. M. Carlson, R. A. Rosell and W. Vallejos, *Anal. Chem.*, 39 (1967) 688.
- 8 T. Ozawa, *J. Chem. Soc. Japan*, 87 (1966) 576.
- 9 E. Pungor, *Oscillometry and Conductometry*, Pergamon Press, Oxford, 1965, p. 182.
- 10 D. B. Aulenbach, *Anal. Chem.*, 27 (1955) 562.
- 11 J. Mayer, E. Hlucháň and E. Abel, *Anal. Chem.*, 39 (1967) 1460.
- 12 *Shimadzu Capillary Type Isotachophoretic Analyser Data Sheet*, Shimadzu, Kyoto, 1980.
- 13 K. Fukushi, G. Kondoh, K. Hiroy, T. Tanaka, A. Kawahara and S. Wakida, *Bunseki Kagaku (Jap. Anal.)*, 32 (1983) 362.
- 14 T. Hirokawa and Y. Kiso, *J. Chromatogr.*, 242 (1982) 227.