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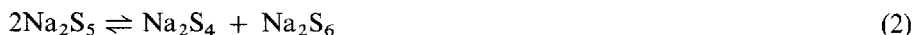
Ion-pair chromatographic separation of inorganic sulphur anions including polysulphide^a

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Aqueous sodium sulphide (Na_2S) dissolves elemental sulphur with the formation of polysulphides (Na_2S_n). The maximum average chain length, n , of the anions is *ca.* 5 at 25°C .^{2,3} and the presence of all polysulphide anions with up to six sulphur atoms has been assumed²⁻⁷. Owing to the rapid autoxidation of both aqueous monosulphide⁸ and polysulphide⁹, such solutions usually contain at least traces of sulphite and thiosulphate in addition:



Polysulphide solutions play an important role in a number of technical processes, in environmental chemistry and in the sulphur metabolism of certain sulphur bacteria such as *Chlorobium*¹⁰ and other species¹¹. The analysis of such solutions is difficult owing to the air sensitivity and the rapid establishment of equilibria of type 2. UV absorption spectroscopy²⁻⁷ and classical gravimetric and titrimetric techniques^{8,12,13} have been applied, but to our knowledge no chromatographic separation has been reported. However, monosulphide, sulphite, sulphate, thiosulphate and thiocyanate have been separated by ion-exchange chromatography¹⁴. This paper is concerned with the ion-pair chromatographic separation of monosulphide, sulphite, thiosulphate, and polysulphide in aqueous solutions and with the autoxidation of such solutions.

EXPERIMENTAL

The compounds $\text{Na}_2\text{S} \cdot 7-9\text{H}_2\text{O}$ (Merck), $\text{K}_2\text{S}_2\text{O}_3$ (purum, Fluka) and Na_2SO_3 (puriss. p.a., Fluka) were purchased in the highest available purity. Elemental sulphur

^a Sulphur compounds, Part 127; for Part 126, see ref. 1.

(Merck DAB 6) was recrystallized from carbon disulphide and consisted entirely of S_8 . To prepare the solutions, either demineralized water ("water 1"), doubly distilled water ("water 2a") or doubly distilled and freshly degassed (in a vacuum) water ("water 2b") was used. The polysulphide solutions were made from freshly recrystallized sodium sulphide (10 g) dissolved in 200 ml of water 2b and 5 g of S_8 by heating and stirring for 2 h under nitrogen. When most of the S_8 had dissolved, 200 ml of water 2b were added and the heating and stirring continued for 1 h, followed by cooling to 20°C and filtration through a glass frit (D2) under nitrogen. To dilute this solution to concentrations suitable for ion chromatography, water 2b that had been adjusted to pH 11 with aqueous sodium hydroxide was used.

The chromatographic equipment consisted of the following components: Varian 5000 pump (microprocessor controlled) or Knauer pump, Valco or Rheodyne loop injector (10 μ l), several UV absorbance detectors (Varian UV5 working at 215 nm, GAT-LCD-501 with variable wavelength and Waters 990 diode-array detector with NEC APC III computer), Hewlett-Packard 3390A electronic integrator, Knauer pen recorder and Waters 990 plotter. The following two columns were found to be equally suitable for the ion-pair chromatography: PRP-1 (Hamilton; 150 mm \times 4.1 mm I.D., particle size 5 μ m) and PLPR-S (Polymer Laboratories; 120 mm \times 4 mm I.D., particle size 8 μ m).

As the composition and stability of polysulphide solutions depend strongly on the pH, the following alkaline eluent of pH \approx 11 was used: 85% (v/v) water 2a, 15% (v/v) acetonitrile (Promochem Chrom AR), 0.001 mol/l sodium carbonate, 0.002 mol/l tetra-*n*-butylammonium hydroxide (purum, Fluka). This mixture was degassed in a vacuum with application of ultrasound. An increase in the acetonitrile concentration reduces the retention times. The eluent flow-rate was varied between 1 and 2 ml/min.

RESULTS

In Fig. 1 the chromatographic separation of sulphide, sulphite, thiosulphate and polysulphide is shown. The assignment of peaks 1–3 to the first three compounds is based on measurements with the pure substances. Freshly recrystallized commercial sodium sulphide (from water 2a) showed a chromatogram with just one peak (Fig. 1A), the height of which was a linear function of the sulphide concentration in the range 0–1.2 mmol/l. The UV spectrum of this substance showed one peak at 231 nm only (range 200–400 nm). In a similar fashion, the integrated peak areas and the heights of the sulphite and thiosulphate peaks were linear functions of the concentrations of the corresponding anions in the concentration range 0–1 mmol/l (see Fig. 2). Potassium thiosulphate was used as it crystallizes without water, while the exact composition of $Na_2S_2O_3 \cdot 5H_2O$ is always uncertain.

The detection limits of sulphite and thiosulphate in a sodium sulphide sample were approximately 0.02% (by weight) for sulphite and 0.01% or 0.2 μ g/ml for thiosulphate. When a solution of elemental sulphur in aqueous sodium sulphide was analysed, the chromatograms shown in Fig. 1B and C were obtained. The assignment of peak 4 to a mixture of polysulphides (S_x^{2-}) is based on the following observations:

(a) the relative height and area of peak 4 increased and simultaneously those of peak 1 decreased when more sulphur was added, which is explained by reaction 1.

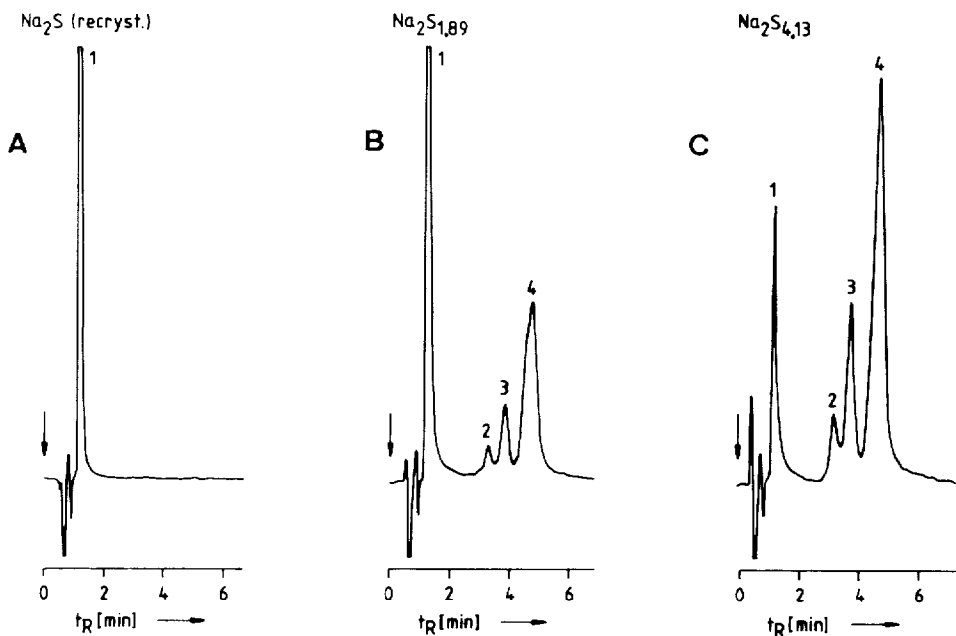


Fig. 1. Chromatograms of (A) freshly recrystallized Na₂S and of two sodium polysulphide solutions of composition (B) Na₂S_{1.9} and (C) Na₂S_{4.1}. Ordinate: absorbance at 215 nm. Peaks: 1, HS⁻; 2, SO₃²⁻; 3, S₂O₃²⁻; 4, S_x²⁻.

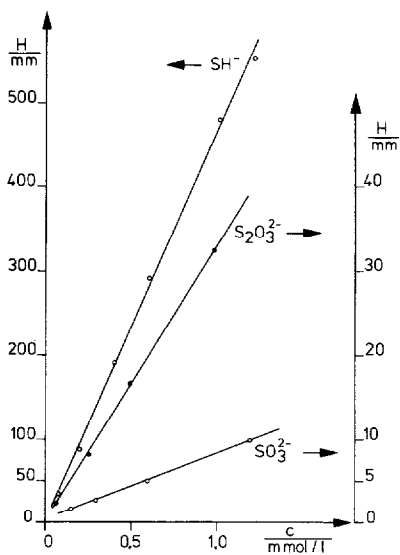


Fig. 2. Calibration functions of sulphide, sulphite and thiosulphate anions; dependence of the chromatographic peak heights as a function of the molar concentrations. As the peak heights also vary with the retention time, the flow-rate and the eluent composition have to be kept constant.

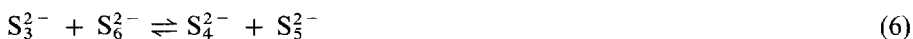
(b) When oxygen was bubbled through the polysulphide solution with simultaneous monitoring of the anion concentrations, it was observed that peaks 1, 2 and 4 decreased and finally disappeared whereas peak 3 increased, which can be explained by reactions 3, 4 and 5



Sulphate does not absorb at 215 nm and therefore does not show up in the chromatograms.

(c) Using the diode-array detector, an absorption spectrum of the substance represented by peak 4 was recorded (see Fig. 3). The spectrum observed is characteristic of a dilute polysulphide solution²⁻⁷ and distinctly different from the spectrum of S_8 ¹⁵. Especially the broad absorption maximum at 285 nm is typical of S_x^{2-} , since S_3^{2-} , S_4^{2-} , and S_5^{2-} absorb at this wavelength with large molar absorptivities⁷. Neither SO_3^{2-} nor $\text{S}_2\text{O}_3^{2-}$ absorbs at 285 nm.

The assignment of peak 4 to a mixture of polysulphide anions implies that this mixture is not separated due to rapidly established equilibrium reactions of types 2 and 6.



We tried to achieve at least a partial separation by varying the eluent composition and the polysulphide concentration.

Repeatedly a shoulder on either the left or the right wing of peak 4 was observed and several times a separation into two peaks was observed. The other peaks always remained symmetrical with no indications of shoulders or tails. However, these observations were not always reproducible and therefore just indicate that peak 4 represents a mixture of anions which at present cannot be separated. Under these

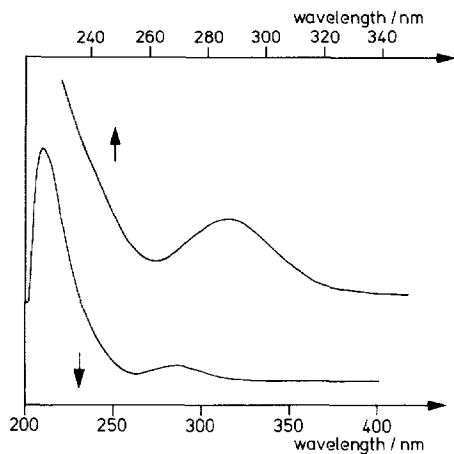


Fig. 3. Absorption spectrum of the substance giving rise to peak 4 in Fig. 1, which is assigned to a mixture of polysulphides, S_x^{2-} . Solvent: acetonitrile-water (15:85, v/v), pH 11. The upper spectrum was recorded with an extended ordinate scale.

circumstances, it does not seem possible to calibrate the height or area of peak 4 *versus* the polysulphide concentration, and only a qualitative and semiquantitative polysulphide analysis is possible.

This chromatographic technique was applied to the analysis of three commercial products of "sodium sulphide, $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ ($x = 7-9$)". These products (Merck) were labelled "reinst", "extra pure" and "pro analysi", respectively. In addition to sulphide, all the samples contained traces of sulphite, thiosulphate and polysulphide. When the samples were dissolved in water 2b and rapidly analysed, between 0.3 and 1.4% (by weight) of thiosulphate and *ca.* 0.2% of sulphite were found. When water 1 was used, slightly higher levels of sulphite and thiosulphate were determined. This indicates that the oxygen dissolved in water 1 produces some additional sulphite and thiosulphate by reactions 4 and 5. This result is in agreement with the observations by Schulek and Körös⁸, who observed the formation of sulphite and thiosulphate by autoxidation of sulphide. However, if oxygen was supplied in excess by bubbling it into the sodium sulphide solution through a sintered-glass frit, all the sulphite and thiosulphate disappeared within 90 min (by oxidation to sulphate), as did polysulphide. Obviously reaction 5 is faster than reaction 4 under these conditions. The pH of these solutions was approximately 13.

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