

CHROMATOGRAPHIC STUDIES ON SULPHUR COMPOUNDS

PART V. A STUDY TO SEPARATE THIOSULPHATE, SULPHITE AND THE LOWER POLYTHIONATES BY ANION-EXCHANGE CHROMATOGRAPHY

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Anion-exchange chromatography has proved such a powerful technique for the separation of homologous series or closely-related inorganic anions, *e.g.* polyphosphates^{1,2}, lower phosphorous acids³, and the imido-ring and chain phosphates⁴⁻⁶, that it was decided to attempt to separate the polythionates using this technique. Work had already been carried out in these laboratories⁷ using both strongly and weakly basic anion-exchangers, but of unspecified cross-linkages, and assumed to be about 10% from swelling characteristics. Using the former resin, thiosulphate was eluted with both *N* and 3*N* sodium chloride solution. Trithionate and tetrathionate could not be eluted with such solvents, buffered at, pH 4 or pH 2, or unbuffered, or with 2*N* sulphuric acid. With the weakly basic resin, tetrathionate was eluted very slowly with 3*N* sodium chloride, not at all with citric acid, and very slowly with 0.5*N* and 2*N* sulphuric acid. 6*N* hydrochloric acid eluted tetrathionate but slowly from both resins, and concentrated hydrochloric acid eluted both these thionates, but too rapidly for a separation to occur.

While the present research was in progress, IGUCHI⁸ published results showing a separation of the thionic acids using an anion-exchange column of Dowex-1, 2% cross-linked D.V.B.* IGUCHI⁸ also reported a separation of sulphite, sulphate, sulphide and thiosulphate, using different solvents. Since polythionates are usually found together with thiosulphate and sulphite in mixtures, these separations are of limited use. A separation of polythionates, sulphite and thiosulphite is desirable.

Anion-exchange chromatography has the advantage over paper chromatography, in that relatively large volumes of solution at high concentrations can be used.

EXPERIMENTAL

Salts

- (1) AnalaR sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.
- (2) AnalaR sodium sulphite $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$.
- (3) Potassium trithionate, for preparation see ref. 9.
- (4) Potassium tetrathionate, for preparation see ref. 10.
- (5) Potassium pentathionate, for preparation see ref. 11.

* Divinylbenzene.

Determination

The thiosulphate and sulphite were estimated in the collected 5 ml fractions, using the conventional iodine titration method. When thiosulphate and sulphite occurred together, the sulphite was complexed with formaldehyde, and the thiosulphate determined alone; the sulphite figure being obtained by difference.

The method used for the determination of the polythionates¹² was titration under Andrew conditions, *i.e.* direct titration with standard potassium iodate solution, in the presence of 6*M* hydrochloric acid and carbon tetrachloride.

Anion-exchange chromatography

Resin: De-Acidite FF, Water regain 1.6–2.00 (cross-linkage D.V.B. 2%), mesh size 52–100 B.S.S.

Column: 20 cm long × 0.75 cm² cross-section area. The column after packing was washed well with 9*M* hydrochloric acid and finally with water.

TABLE I

Solvent (<i>M</i> HCl)	Volume used (ml)	Trithionate		Tetrathionate		Pentathionate	
		S.V.	F.V.	S.V.	F.V.	S.V.	F.V.
3	75	35	70	—	—	—	—
6	65	—	—	95	110	—	—
9	50	—	—	—	—	145	180
Concentration of thionate applied (mmol)		0.04		0.04		0.04	
% Recovery		100 ± 1		101 ± 2		98 ± 1.5	

S.V. = Break through or appearance volume of species.

F.V. = Final or disappearance volume of species.

Conditions of elution

The conditions for elution (see Table I) are by a batch method, since optimum elution conditions for each species are so different that gradient elution proved inefficient. A typical separation is shown in Fig. 1, while Fig. 2 shows the elution of trithionate under identical conditions, but using an 8% D.V.B. cross-linked resin.

Since the separation of the polythionates was satisfactory, a separation of sulphite and thiosulphate was sought. The final solvent used was a solution of 2*M*

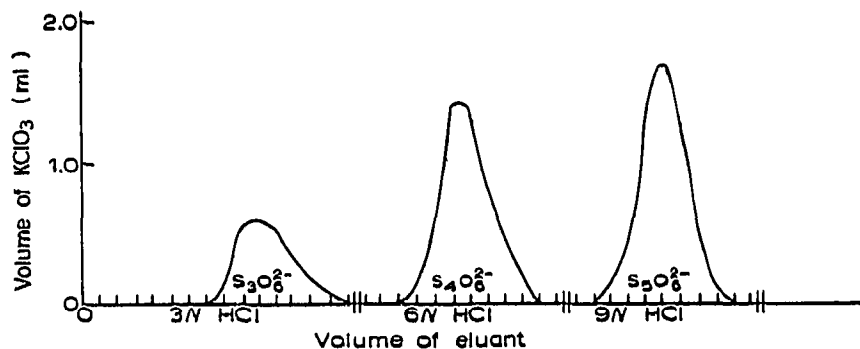


Fig. 1. Elution of the polythionates from a De-Acidite FF 2% D.V.B. cross-linked resin.

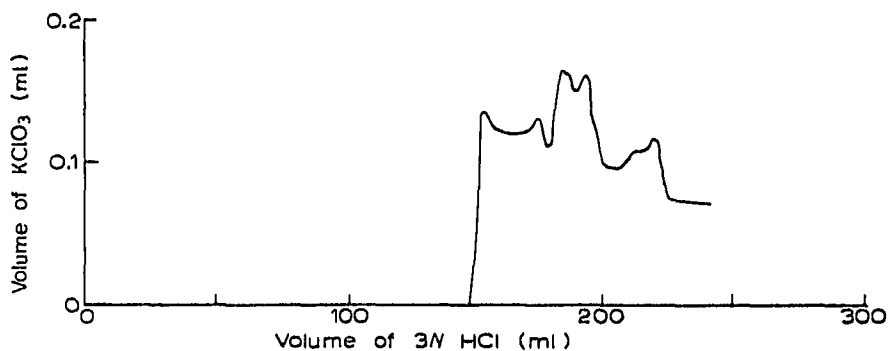


Fig. 2. Elution of trithionate from an 8% D.V.B. cross-linked resin.

potassium hydrogen phthalate ($\text{pH} = 4$). Carefully controlled experiments showed that the polythionates and thiosulphate were stable in this media for much longer periods of time than that taken for the anion-exchange separation. However, when the separation of thiosulphate and trithionate was attempted, a complication arose. On changing the solvent after elution of the thiosulphate, and passing $3M$ hydrochloric acid through the column, free phthalic acid was produced and the column was blocked. Thus after passage of the phthalate buffer, a further buffer, $\text{pH} 4$, made up of sodium acetate-hydrochloric acid was also passed down the column, to remove the phthalate buffer.

By combination of these two methods, the separation shown in Figs. 3 and 4 was achieved, with the conditions given in Table II.

Fig. 3 shows the complete separation, while Fig. 4 gives the total graph of $\text{SO}_3^{2-} + \text{S}_2\text{O}_3^{2-}$, and also the $\text{S}_2\text{O}_3^{2-}$ only, whilst Fig. 4b gives the resultant elution patterns of SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ when the $\text{S}_2\text{O}_3^{2-}$ contribution is subtracted from the $\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-}$ graph.

The behaviour of hexathionate in $9M$ HCl was studied, and although it is sepa-

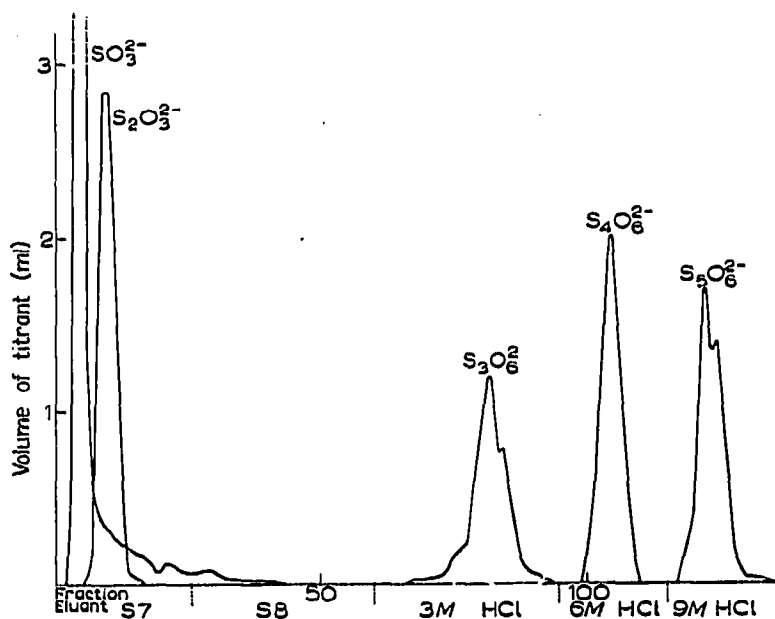


Fig. 3. Elution of polythionates, sulphite and thiosulphate from a 2% cross-linked resin.

TABLE II

Eluants	Ion eluted
(1) 250 ml of 2 M potassium hydrogen phthalate (S7)	SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$
(2) 250 ml of sodium acetate-hydrochloric acid buffer, pH 4 (S8)	—
(3) 250 ml of 3 M HCl	$\text{S}_3\text{O}_6^{2-}$
(4) 250 ml of 6 M HCl	$\text{S}_4\text{O}_6^{2-}$
(5) 250 ml of 9 M HCl	$\text{S}_5\text{O}_6^{2-}$

rated from pentathionate, tailing of the peak was noted. Work is in progress to correct this phenomenon, then it is hoped to apply this method to study reactions where these ions are found.

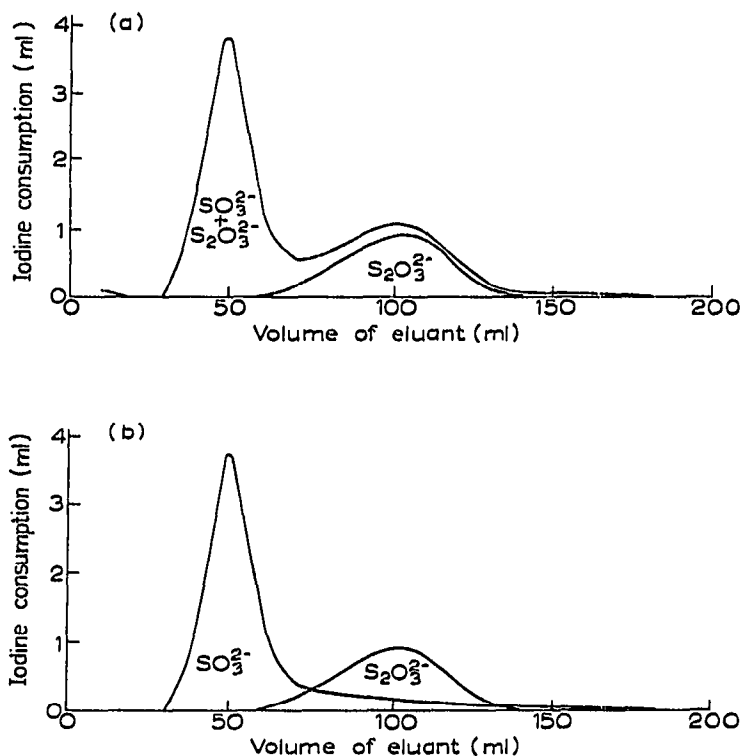


Fig. 4. (a) Elution of sulphite and thiosulphate from a 2% cross-linked resin. (b) Elution of sulphite and thiosulphate from a 2% cross-linked resin, calculated from (a).

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SUMMARY

A method has been devised for the analysis of sulphite, thiosulphate, trithionate, tetrathionate and pentathionate by anion-exchange chromatography.

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