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## Note

### Ion-pair chromatographic separation of polythionates $S_nO_6^{2-}$ with up to thirteen sulphur atoms\*

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The polythionates, or sulphanedisulphonates, containing the anions  $S_nO_6^{2-}$  ( $n > 2$ ), play an important role in a number of technical processes, in environmental chemistry, in the sulphur metabolism of certain sulphur bacteria and generally in many basic reactions of inorganic sulphur chemistry. Therefore, the analytical chemistry of these anions has been studied repeatedly (for reviews, see refs. 2 and 3), and recently a number of publications dealing with the high-speed liquid chromatography of polythionates has appeared<sup>4–10</sup>. Quite different chromatographic techniques and conditions have been used in these investigations and polythionates with up to six sulphur atoms in the molecule have been separated and detected. Still higher  $S_nO_6^{2-}$  ions with up to nine sulphur atoms have been separated by paper ionophoresis<sup>11</sup>.

We report here for the first time the separation and detection of polythionate anions with up to thirteen sulphur atoms by ion-pair liquid chromatography.

#### EXPERIMENTAL

The crystalline compounds  $K_2S_3O_6$ ,  $K_2S_4O_6$ ,  $K_2S_5O_6 \cdot 1.5H_2O$  and  $K_2S_6O_6$  were prepared by published methods<sup>12,13</sup> according to the following equations:

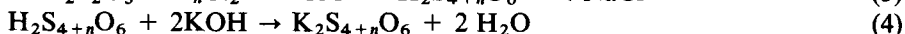
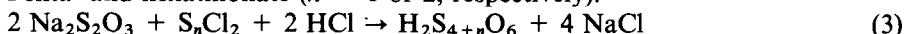
Trithionate:



Tetrathionate:



Penta- and hexathionate ( $n = 1$  or  $2$ , respectively):



The chromatographic systems used consisted of the following components: Varian 5000 pump (microprocessor controlled) or Knauer pump, Valco or Rheodyne loop injector (10  $\mu$ l) and a UV detector (Knauer type 71.79 working at 254 nm or Varian UV 5 at 215 nm, respectively) connected to a Hewlett-Packard 3390 A elec-

\* Sulphur compounds, Part 100; for Part 99 see ref. 1.

tronic integrator and a Knauer pen recorder. Two different columns were used: (1) a Dionex MPIC-NS 1 column (stationary phase polystyrene-divinylbenzene) of dimensions  $200 \times 5$  mm I.D., and (2) a Chrompack cartridge glass column (stationary phase CP<sup>TM</sup> SpherC<sub>18</sub>) of dimensions  $100 \times 3.0$  mm I.D. Because it turned out that the retention time of polythionate anions depends on the square of the number of sulphur atoms in the molecule, three different eluent compositions had to be employed: (1) 27% acetonitrile (Promochem ChromAR), 4% methanol (freshly distilled from magnesium sulphate), 69% water (distilled twice), 0.001 M sodium carbonate (p.a.) and 0.002 M tetra-*n*-butylammonium hydroxide (purum, Fluka); (2) 40% acetonitrile, 60% water, 0.001 M sodium carbonate, 0.002 M tetra-*n*-butylammonium hydroxide; (3) 30% acetonitrile, 70% water, 0.002 M tetra-*n*-butylammonium dihydrogen phosphate, 0.001 M sodium carbonate (pH of this mixture *ca.* 7). Eluents 1 and 2 were used with column 1 to produce the chromatograms in Fig. 1a and b, respectively, and eluent 3 was used with column 2 for the quantitative analysis shown in Fig. 2. The eluent flow-rate was 1 ml/min throughout.

## RESULTS

In Fig. 1a the chromatographic separation of thiosulphate and the polythionate anions with three to six sulphur atoms is shown. The peak identification caused no problems since all compounds were available as pure or almost pure substances. The retention times and capacity factors ( $k'$ ) obtained with column 1 and eluent 1 are listed in Table I. From the data in this table it follows that  $\ln k'$  is a linear function of the square of the number ( $n$ ) of sulphur atoms in the molecule (except,

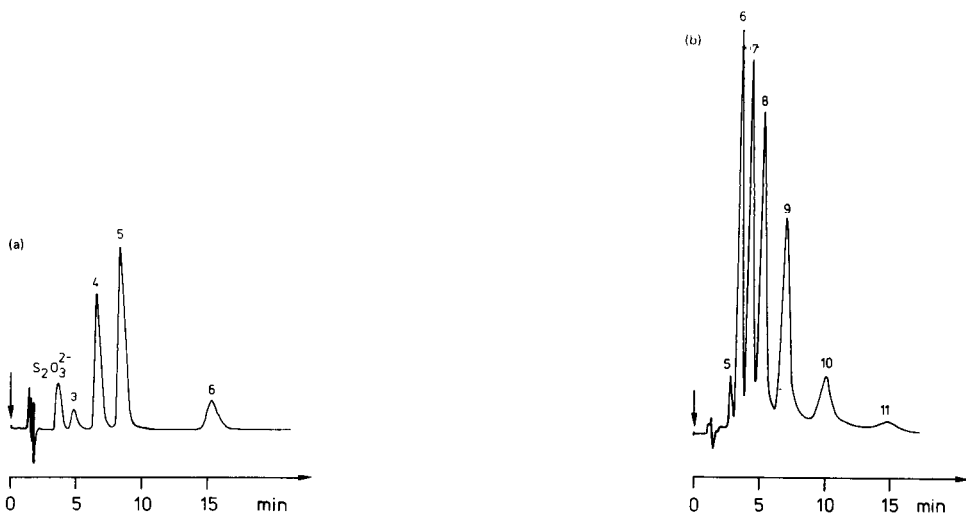


Fig. 1. (a) Separation of thiosulphate and the lower polythionates  $S_3O_6^{2-}$ ,  $S_4O_6^{2-}$ ,  $S_5O_6^{2-}$  and  $S_6O_6^{2-}$  (column 1, eluent 1, detection at 254 nm). (b) Separation of the higher polythionates from  $S_5O_6^{2-}$  to  $S_{11}O_6^{2-}$  (column 1, eluent 2). The figures give the number of sulphur atoms in the anion. For retention times see Table I; shown is the detector response at 254 nm.

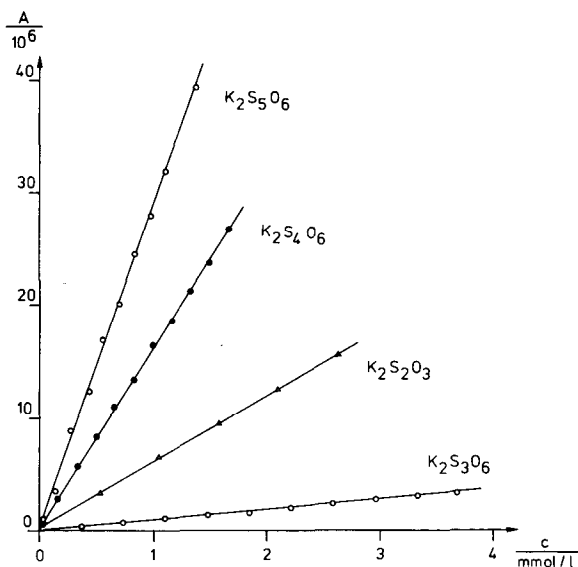


Fig. 2. Calibration functions  $c_i = f(A_i)$  for the polythionates  $S_3O_6^{2-}$ ,  $S_4O_6^{2-}$  and  $S_5O_6^{2-}$  as well as for  $S_2O_3^{2-}$  (column 2, eluent 3);  $A_i$  = integrated peak area, based on the absorbance at 215 nm;  $c_i$  = molar concentration of species  $i$ .

of course, the thiosulphate anion). The following parabolic relationship was obtained (linear correlation coefficient,  $r = 0.994$ ):

$$\ln k' = 0.4976 + 0.05063n^2$$

For the separation of higher polythionate anions ( $n > 6$ ) eluent 2 was used. To prepare a mixture containing such anions, dichloroheptasulphane ( $S_7Cl_2$ ) was prepared from  $S_7$  and elemental chlorine<sup>14,15</sup> and treated with  $Na_2S_2O_3$  according

TABLE I

RETENTION TIMES,  $t_R$  (min), AND CAPACITY FACTORS,  $k'$ , OF POLYTHIONATE IONS UNDER DIFFERENT CONDITIONS

	Column 1, eluent 1			Column 1, eluent 2		
	$t_R$	$k'$	$\ln k'$	$t_R$	$k'$	$\ln k'$
$S_3O_6^{2-}$	4.64	2.57	0.944	—	—	—
$S_4O_6^{2-}$	6.42	3.94	1.371	—	—	—
$S_5O_6^{2-}$	8.22	5.32	1.672	2.96	0.910	-0.095
$S_6O_6^{2-}$	15.04	10.57	2.358	3.52	1.271	0.240
$S_7O_6^{2-}$				4.33	1.794	0.584
$S_8O_6^{2-}$				5.26	2.394	0.873
$S_9O_6^{2-}$				7.00	3.516	1.274
$S_{10}O_6^{2-}$				10.06	5.490	1.703
$S_{11}O_6^{2-}$				14.66	8.458	2.135
Dead time	1.30			1.55		

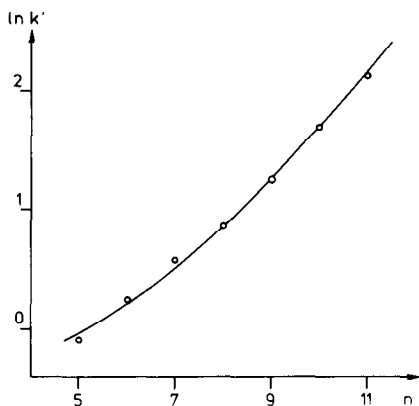


Fig. 3. Dependence of  $\ln k'$  of polythionate anions  $S_nO_6^{2-}$  ( $n = 5-11$ ) on the number of sulphur atoms in the molecule (column 1, eluent 2; for data see Table I).

to eqn. 3 and following the procedure of the pentathionate preparation<sup>13</sup>. The purity of the  $S_7Cl_2$  was checked by treatment with titanocene pentasulphide to produce the corresponding sulphur homocyclic rings<sup>15</sup> (e.g.  $S_{12}$  from  $S_7Cl_2$  and  $Cp_2TiS_5$ ) followed by reversed-phase HPLC analysis of the mixture. In this way it was found that besides  $S_7Cl_2$  comparable amounts of other dichlorosulphanes  $S_nCl_2$  ( $n = 2-6$ ) were present but the concentration of species  $S_nCl_2$  with  $n > 7$  must have been smaller by about one order of magnitude since the peaks due to  $S_{13}$ ,  $S_{14}$ , etc. were much smaller than those due to  $S_7-S_{12}$ .

Treatment of this chlorosulphane mixture with  $Na_2S_2O_3$  produced the polythionate mixture shown in Fig. 1b, showing  $S_{11}O_6^{2-}$  to be the largest anion, which must have resulted from  $S_7Cl_2$  according to eqn. 3. The retention times and capacity factors  $k'$  are listed in Table I, the non-linear dependence of  $\ln k'$  on the number ( $n$ ) of sulphur atoms is shown in Fig. 3. The data can be fitted to the parabolic relationship (correlation coefficient:  $r = 0.999$ ):

$$\ln k' = -0.598 + 0.0229n^2$$

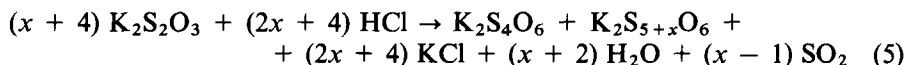
It is obvious from the data in Table I that polythionates with more than ten sulphur atoms should be analysed with eluents that have a lower concentration of the ion-pair reagent  $N(C_4H_9)_4^+$ . We have therefore analysed the mixture resulting from the reaction between  $S_7Cl_2$  and  $Na_2S_2O_3$  by a gradient technique lowering the concentration of tetra-*n*-butylammonium dihydrogen phosphate within 10 min from 0.001 *M* to 0.0002 *M* and the concentration of sodium carbonate from 0.0005 *M* to 0.0001 *M* (water-acetonitrile, 70:30). After 10 min the eluent composition was kept constant. Under these circumstances  $S_{11}O_6^{2-}$  arrived at the detector after ca. 14 min, and additional peaks due to  $S_{12}O_6^{2-}$  (ca. 18 min) and  $S_{13}O_6^{2-}$  (ca. 30 min) were observed with peak areas approximately equal to that of  $S_{11}O_6^{2-}$ .

For a quantitative interpretation of the chromatograms in Fig. 1 the correlation between the integrated peak area  $A$  and the molar concentration  $c_i$  has to be known for each species. Therefore, the calibration functions  $c_i = f(A_i)$  have been determined using the pure compounds  $K_2S_3O_6$ ,  $K_2S_4O_6$ ,  $K_2S_5O_6 \cdot 1.5H_2O$  as well

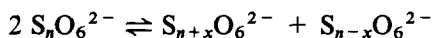
as  $K_2S_2O_3$ . Column 2 and eluent 3 were used and the UV absorbance at 215 nm was recorded in this case. The results are shown in Fig. 2. All four calibration functions are linear within a wide concentration range, and the slope of the curves obtained for the  $S_nO_6^{2-}$  anions increases with the number of two-coordinate sulphur atoms in the molecule, which is reasonable and in agreement with the published UV spectra<sup>16</sup> of these compounds.

In search for still longer-chain polythionates we have investigated the products of the decomposition of potassium thiosulphate by hydrochloric acid which, according to Weitz and Spohn<sup>17</sup>, contain polythionate anions with up to twelve sulphur atoms. Since these species cannot be separated by fractional crystallization, the evidence for the higher polythionates ( $n > 6$ ) obtained by Weitz and Spohn<sup>17</sup> is only indirect and rests on the high sulphur content of the crystalline products obtained by cooling and partial evaporation of the aqueous solutions.

Following the procedure on p. 2339 of ref. 17,  $K_2S_2O_3$  was treated with aqueous hydrochloric acid at  $-10^\circ C$  in the presence of arsenic trioxide. After filtration from the precipitated potassium chloride and arsenic trisulphide and evaporation of most of the water and hydrochloric acid, the yellowish oily liquid phase was analysed by ion-pair liquid chromatography (column 1, eluent 2). The chromatograms showed the presence of all polythionates from  $S_4O_6^{2-}$  to  $S_{10}O_6^{2-}$ , with the corresponding peak areas decreasing with increasing number of sulphur atoms per molecule indicating a sharp drop in concentration in that order. These results confirm the conclusions arrived at by Weitz and Spohn<sup>17</sup>. The most likely reaction to explain the formation of higher polythionates from thiosulphate is shown in eqn. 5 with  $x = 1, 2$ , etc.:



In the above-mentioned preparation of hexathionate from thiosulphate and dichlorodisulphane<sup>13</sup> all polythionates with up to eleven sulphur atoms were observed by ion-pair liquid chromatography. It therefore seems that the formation of  $S_nO_6^{2-}$  anions with  $n = 3-11$  in various types of reaction is quite common, and that interconversion reactions of the type



must take place at moderate temperatures. Acidic aqueous solutions of the sodium salts of these anions have been found to be stable for weeks at  $25^\circ C$ .

#### ACKNOWLEDGEMENTS

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