ION CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF SOME SULPHUR ANIONS

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An ion chromatographic method was developed for the simultaneous determination of sulphate, thiosulphate, trithionate, and tetrathionate using Separon HEMA ion exchangers based on hydroxyethyl methacrylate gels. Sulphate and thiosulphate were detected by indirect photometry at 254 nm, trithionate and tetrathionate, treated separately on another chromatograph, were detected by direct photometry at 205 nm. The method was applied with success to the study of the oxidation of thiosulphate in conditions of carbonate leaching.

During the carbonate leaching of sulphide ores, sulphide is oxidized to thiosulphate and ultimately to sulphate. Polythionates, particularly trithionate and tetrathionate, are formed during this process as intermediates, which have a detrimental poisoning effect on anion exchanger resins that are used in the subsequent workup.

We examined the oxidation of thiosulphate by air under conditions modelling carbonate leaching with a view to gaining insight into the mechanism of the thiosulphate oxidation and factors influencing the formation of polythionates[1].

Carbonate leaching solutions contain up to 30 g l^{-1} carbonate or bicarbonate, up to 4 g l^{-1} chloride and ammonium ions and several mg l^{-1} complexed copper(II) ions. Sulphate, thiosulphate, trithionate and tetrathionate are present in total concentrations of 0–1 g l^{-1} (calculated as sulphur). In our study, samples were taken in 30 min intervals, and with regard to the poor stability of polythionates, they had to be analyzed immediately.

The separation and determination of polythionates in the presence of other sulphur oxo anions is very difficult. A convenient technique for this purpose is ion chromatography. The first to use this technique for the separation of polythionates were Wolkoff and Larosse[2], and other studies followed[3–6], but none of the procedures developed is directly applicable to the analysis of carbonate leaching solutions.

The capacity ratios of the anions to be determined are different to such an extent that conditions for the isocratic elutions of all of them cannot be established. Moreover, sulphate can be detected photometrically only indirectly[7], so that the use of gradient elution is also impossible.

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With respect to the instrumentation available, we have worked out a method where two chromatographs are simultaneously employed: one, for the determination of sulphate and thiosulphate using indirect photometric detection at 254 nm, the other, for the determination of trithionate and tetrathionate using direct photometric detection at 205 nm. Details of the procedure are given in this paper.

EXPERIMENTAL

Chemicals and Solutions

The chemical used were of reagent grade purity (Lachema, Brno), solutions were prepared using redistilled water. Eluents were made up from the following stock solutions: sodium perchlorate 1 mol l^{-1}, sulphosalicylic acid 0·05 mol l^{-1}, phosphate buffer pH 6·0, 0·5 mol l^{-1} with respect to phosphate. Their pH was adjusted with sodium hydroxide and the eluents were filtered through a Synpor No 3. membrane filter (Lachema, Brno) immediately before use.

Standard solutions for calibration were prepared daily using the same concentratios of carbonate, bicarbonate, chloride and ammonium ions as in the actual reaction mixtures. Trithionate standard was prepared following ref.[8], its purity by cerimetric titration[9] was 95% and no thiosulphate or tetrathionate was found by ion chromatography under the conditions used. Tetrathionate was prepared in the solutions by titration of a known amount of thiosulphate with the equivalent amount of iodine.

Sorbents

Separon H 1000 DEtA sorbent, $d_p = 15-25$ μm, $Q_g = 1$ mmol g^{-1}, was prepared from Separon HEMA 1000 containing 1 mmol g^{-1} epoxy groups (Laboratorní přístroje, Prague) by reacting it with triethanolamine[10]. Diethamolaminoethyl groups are assumed to be the functional groups of this sorbent.

Separon HEMA 300 DEAE sorbent, $d_p = 13-21$ μm, $Q_g = 0{\cdot}5$ mmol g^{-1}, was a product of Laboratorní přístroje, Prague.

The glass columns were packed with the sorbents by using the slurry method described in ref.[10].

Chromatographic Treatment

The chromatographic equipment and conditions for the determination of trithionate and tetrathionate were as follows. A VCM 300 pump (Development Workshop, Czechoslovak Academy of Sciences in Prague), LCI 02 septum type injector (Laboratorní přístroje, Prague), CGC compact glass column 150 × 3·3 mm in a PKS 1 column holder (Laboratorní přístroje, Prague), Model 87·00 spectrophotometric detector (Knauer, Oberursel, F.R.G.), TZ 4200 line recorder (Laboratorní přístroje, Prague), sorbent: Separon H 1000 DEtA, eluent: sodium perchlorate with an addition of phosphate buffer $c_{(NaClO_4)} = 25$ mmol l^{-1}, $c_{(PO_4^{3-})} = 5$ mmol l^{-1}, pH 6·0, flow rate 1 ml min^{-1}, pressure 1·5—4 MPa; detection: direct photometry at 205 nm, sensitivity 0·04 AUFS, sample volume 5 μl injected by using a 701 N microsyringe (Hamilton, Reno, U.S.A.).

For sulphate and thiosulphate the equipment and conditions were as follows. An MMC pump (Mikrotechna, Prague), injector, column and line recorder as above, detector: a 254/280 nm photometer (Varian, Palo Alto, U.S.A.), sorbent: Separon H 300 DEAE, eluent: sulphosalicylic acid 0·05 mmol l^{-1} neutralized with NaOH to pH 6·0, flow rate 1·5 ml min^{-1}, pressure 1·5 to

4 MPa; detection: indirect photometry at 254 nm, sensitivity 0·02—0·04 AUFS, sample volume 5 μm.

The concentrations of the anions wre calculated from the peak heights.

RESULTS AND DISCUSSION

Because of the high ionic concentration of the solutions analyzed, sorbents with a relatively high exchange capacity had to be used for the chromatographic treatment of the carbonate leaching liquors; this in turn compelled the use of a highly potent eluting agent, containing perchlorate and sulphosalicylate anions.

Examples of the chromatographic separation are shown in Fig. 1*a*,*b*. Initially, Separon HEMA 300 DEAE was used not only for the separation of sulphate and thiosulphate but also for the separation of trithionate and tetrathionate. However, taking into account the results obtained by Vláčil and Vinš[11], Separon HEMA 300 DEAE was later replaced by Separon H 1000 DEtA in the latter case. This sorbent gives a better resolution in a shorter time under otherwise identical conditions, and thiosulphate is even resolved from other anions, nitrate and iodide in particular, thus making for a more sensitive determination of this anion. The separation of polythionates on this sorbent is shown in Fig. 1*c*. The last peak 11 is presumably pentathionate, its identity, however, was not verified.

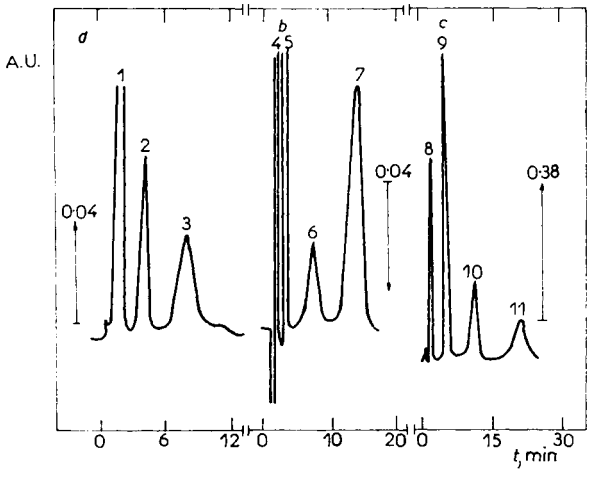

FIG. 1

Determination of trithionate and tetrathionate (*a*), of sulphate and thiosulphate (*b*), and separation of polythionates in a solution of decomposed trithionate (*c*). For chromatographic conditions see the text. Peaks: 1 $S_2O_3^{2-}$, 2 $S_3O_6^{2-}$, 3 $S_4O_6^{2-}$, 4 HCO_3^-, 5 Cl^-, 6 SO_4^{2-}, 7 $S_2O_3^{2-}$, 8 $S_2O_3^{2-}$, 9 $S_3O_6^{2-}$, 10 $S_4O_6^{2-}$, 11 $S_5O_6^{2-}$

The parameters of the method developed are given in Table I. The data, however, are to be regarded as approximate only because the parameters depend on the column capacity and efficiency, which varied with time. On average, 95–105% of sulphur added to the system as thiosulphate was determined as the sum of sulphate, thiosulphate, trithionate and tetrathionate. Taking into account the possible presence of undetected forms of sulphur (sulphite in particular) and volume changes of the system, the accuracy of the method can be regarded as fairly good.

The procedure is very easy to carry out, the sample is injected directly on column. The run time is shorter that 15 min, thus allowing standard to be run after each sample.

The capacity ratios of the sulphate and thiosulphate ions were significantly dependent on the carbonate or bicarbonate concentration in the sample. This can be explained in terms of an increased pH in the sample zone, bringing about a suppression of the functional group protonation and lowering of the effective column capacity. This effect was compensated by using standard solutions containing the same matrix as the actual reaction mixture.

An unidentified peak lying between the peaks of trithionate and tetrathionate was occasionally observed in the chromatograms. This is presumably a system peak[12] whose nature is difficult to fully explain. The height of this peak decreased usually slowly with time during a day work. In contrast to the peaks of trithionate and tetrathionate, the capacity ratio of this peak could be easily varied by minor changes in the eluent pH to achieve a satisfactory resolution from the former anions.

TABLE I
Parameters of determination

Anion	Sensitivity[a] mmol mg^{-1}	Correlation coefficient[b]	Detection limit[c] $mg\ l^{-1}$	RSD[d] %
SO_4^{2-}	0·5	0·995	8	2
$S_2O_3^{2-}$	0·1	0·987	40	3
$S_3O_6^{2-}$	0·3	0·994	3·3	2
$S_4O_6^{2-}$	1·5	—	0·6	4

[a] Calculated as sulphur, slope of the calibration curve set up from four points, each measured in duplicate; [b] correlation coefficient of the calibration curve; [c] concentration (calculated as sulphur) giving a signal equal to the double maximum noise level; [d] relative standard deviation of peak height for ten measurements performed within a working day on an $1\ g\ l^{-1}$ anion standard.

The lifetime of a column was typically about 100 working hours, *i.e.*, 400 injections; after this time the column efficiency and permeability decreased. This relatively short lifetime can be attributed to the non-optimal packing procedure[10], low mechanical strength of sorbent and application of unfiltered samples. However, four or five columns can be re-packed easily in the laboratory within a single working day with only minor equipment demands.

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