

Determination of phosphate in samples with high levels of sulphate by ion chromatography[☆]

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ABSTRACT

A comparative study of the separation of phosphate from chloride, nitrate, nitrite, bromide and sulphate by ion chromatography with direct conductimetric detection and indirect photometric detection was performed. The best resolution was obtained using borate–gluconate or hydrogenphthalate as the eluent. Indirect photometry using hydrogenphthalate or naphthalenedisulphonate gave the best detection limit for phosphate (1 ng). The use of ion-exchange resins in the barium form for the elimination of high levels of sulphate prior to the determination of trace amounts of phosphate was evaluated. For the elimination of sulphate in samples containing less than 1000 mg/l ($\text{SO}_4^{2-}:\text{PO}_4^{3-} = 100$) the column mode can be used, but for samples with high concentrations of sulphate (5000 mg/l) the batch procedure is recommended. The behaviour of commercial cartridges in the barium form was also evaluated. The method was applied to the separation and determination of anions in saline sediments.

INTRODUCTION

The determination of trace components in the presence of major interferents is a common challenge in many areas of analytical chemistry. In ion chromatography (IC) the difficulty becomes particularly severe when the sample is contaminated with high levels of ionic species. Although it may be possible to separate the ionic matrix components from the analyte, this separation becomes difficult to achieve when the concentration of the matrix ions is high because they are eluted as very large peaks, which may obscure the analyte ions and induce retention time variability and loss of chromatographic efficiency. Moreover, high concentrations of ionic compounds result in overloading of the analytical column and shortening of the column lifetime.

Several approaches have been suggested to overcome these adverse effects of high levels of interfering ions. First, the concentration of the matrix ions in the sample can be reduced prior to the analysis by using a suitable precolumn filled with an ion-exchange resin [1,2], hollow-fibre ion-exchange membranes [3] or dialysis through membranes [4]. Other approaches to eliminate matrix contaminants use on-line heart-cutting or recycling methods [5,6]. The use of the interfering ion as the eluent has also been proposed [7]. All these methods are recommended for the elimination of large amounts of chloride in different kinds of sample such as brine [3,8] or sea and polluted water [2,9]. Few methods have been proposed for the elimination of sulphates in highly saline samples, but the use of precolumns in the barium form is generally recommended [10,11]. Few data about their removal capacity or the recoveries of other anions, particularly phosphate, that can coprecipitate or be adsorbed in the resin have been published. In this study the use of precolumns with ion-exchange resins

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in the barium form for the reduction of the sulphate concentration in saline samples before phosphate determination is described.

The determination of phosphate by IC is generally carried out using either direct conductimetric detection in a suppressed system [12] or a non-suppressed system with a low-capacity anion-exchange column and borate–gluconate as eluent [13]. Alternatively, it is possible to use indirect photometric detection with a dilute solution of an aromatic acid anion such as benzoate or phthalate as the eluent [14,15]. Recently, the use of naphthalenesulphonates as mobile phases for anion-exchange chromatography with indirect photometric detection has also been described [16–20], but no information is available about the behaviour of phosphate using these eluents. The applicability of different detection methods for the determination of low concentrations of phosphate was also investigated.

It is generally accepted that phosphate has an important role as nutrient in aquatic systems and its presence could be related to the growth of organisms that can live in hypersaline media. The applicability of the optimized procedure to the determination of phosphate in saline sediments with large amounts of chloride or sulphate is demonstrated.

EXPERIMENTAL

Instruments

The liquid chromatograph consisted of an LKB (Bromma, Sweden) Model 2150 pump, a Rheodyne (Cotati, CA, USA) Model 7125 valve (100- μ l loop), a Metrohm (Herisau, Switzerland) Model 690 conductivity detector, an Applied Biosystems (Foster City, CA, USA) Model 757 UV detector and a W + W recorder. The analytical columns used were a Waters (Milford, MA, USA) IC Pak A (50 \times 4.6 mm I.D.) packed with a methacrylate-based anion exchanger of 30 \pm 3 μ equiv/ml capacity and a Vydac 302 IC (250 \times 4.6 mm I.D.) packed with a silica-based anion exchanger.

Materials

Salts of the common anions, of analytical-

reagent grade or better, were obtained from different suppliers. A 1000 mg/l stock solution of each anion was prepared and used for further dilutions. Water purified using a Culligan water-purification system and filtered through a 0.45- μ m membrane filter was used for all solutions.

Sodium gluconate (97%), boric acid, glycerine (87%), potassium hydrogenphthalate, methanesulphonic acid and acetonitrile (HPLC grade) were obtained from Merck (Darmstadt, Germany). Sodium tetraborate was obtained from Carlo Erba (Milan, Italy), 2-naphthalenesulphonic acid of 70% purity, sodium 2-naphthalenesulphonate (NMS) of 90% purity and disodium 1,5-naphthalenedisulphonate (NDS) of 95% purity was obtained from Aldrich (Steinheim, Germany).

Chromatographic conditions

For the determination of nitrate using direct UV detection at 205 nm, a Vydac 302 IC column and 10 mM methanesulphonic adjusted to pH 4.2 with 1 M sodium hydroxide as eluent at 2 ml/min were used.

Non-suppressed ion chromatography using a Waters IC Pak A and borate–gluconate [1.3 mM tetraborate, 5.8 mM boric acid, 1.3 mM gluconate, 5 g/l glycerine (pH 8.5) and 120 ml/l acetonitrile] at 1 ml/min with conductimetric detection was used for the determination of chloride, nitrite, bromide, nitrate, phosphate and sulphate.

Indirect UV absorption detection at 285 nm using a Waters IC Pak A column and 1 mM potassium hydrogenphthalate adjusted to pH 5.5 with 1 M sodium hydroxide as eluent at 1 ml/min and 0.3 mM NMS–acetonitrile (90:10), 0.3 mM 2-naphthalenesulphonic acid–acetonitrile (90:10) and 0.1 mM NDS acetonitrile (90:10) adjusted to pH 10 with 1 M sodium hydroxide as eluents at 1.2 ml/min was used for the determination of chloride, nitrite, bromide, nitrate, phosphate and sulphate. All eluents were prepared daily, filtered and degassed. Further chromatographic conditions are given in the figure captions.

Chloride and sulphate elimination

Chloride elimination was carried out using a

50W-X8 cation-exchange resin in the Ag^+ form, as described elsewhere [21]. For the elimination of sulphate the strong cation-exchange resin Dowex 50W-X8 in the H^+ form (200–400 mesh) (Fluka, Buchs, Switzerland) was converted into the Ba^{2+} form by soaking in a 1 M solution of barium chloride or barium acetate; previously the resin was thoroughly cleaned with water. When the sample clean-up was carried out in the column mode, the resin was packed in a small column (10 × 0.6 cm I.D.) and placed in a suction flask; when the clean-up was carried out in the off-column mode, the resin was dried at 50°C and added to the sample. The resin was regenerated using 1 M sodium hydroxide, barium chloride or barium acetate and thoroughly rinsed in water.

Commercial cartridges of purified polystyrene resin in the Ba^{2+} form from Alltech, Maxi-Clean IC Ba^{2+} (0.5 ml) and Maxi-Clean IC Ba^{2+} Plus (1.5 ml) were also used.

Sample preparation

Saline samples were air dried and crushed before use. Amounts between 0.1 and 1 g, according to the anion concentration, were dissolved in water by shaking for 16 h and analysed by IC for nitrate and chloride.

For the determination of sulphate and phosphate, the standard method for the determination of phosphate in soils [22] was used. Samples of sediments were treated with 1 M HCl by shaking for 16 h and the solution was then centrifuged at 2000 g and neutralized. The excess of chloride was eliminated using a column containing 1 g of 50W-X8 ion-exchange resin in the Ag^+ form. In samples with high concentrations of sulphate (>1000 mg/l), the latter anion was eliminated using the Ba^{2+} ion-exchange resin in the batch mode.

RESULTS AND DISCUSSION

An example of the separation obtained using the Waters IC Pak A polymeric ion-exchange column and hydrogenphthalate as eluent is shown in Fig. 1. The results are in agreement with those published by Sosimenko and Haddad [23] and Haddad and Cowie [24]. For phosphate

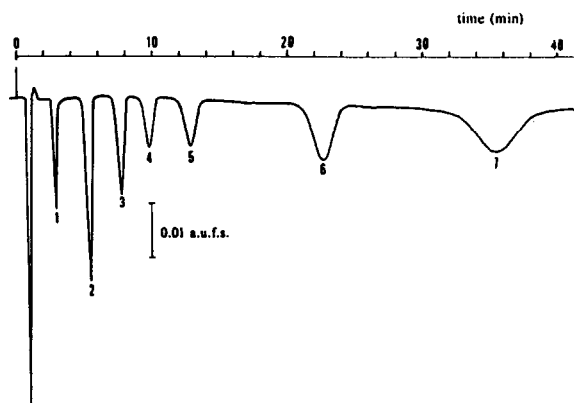


Fig. 1. Separation of a standard mixture of inorganic anions. Peaks: 1 = H_2PO_4^- ; 2 = Cl^- ; 3 = NO_2^- ; 4 = Br^- ; 5 = NO_3^- ; 6 = SO_4^{2-} ; 7 = system peak. Column, Waters IC Pak A; eluent, 1.0 mM potassium hydrogenphthalate (pH 5.5); flow-rate, 1.0 ml/min; indirect UV detection at 285 nm; sample, 100 μl , 10 mg/l.

a distinct increase in k' at pH 7.5–8 was observed, reflecting the presence of high concentrations of the monohydrogenphosphate ion in the sample (monohydrogen phosphate was eluted at higher k' than the dihydrogenphosphate). The system peak showed a decrease when the eluent pH was increased from 4.5 to 5.5; its height became progressively lower and the peak disappeared at pH 7. These results are in agreement with those published by Jackson and Haddad [25] and Karlson and Frankenberg [26] for other anion chromatographic columns and may be related to the pK_a of the phthalic acid ($\text{pK}_1 = 2.95$; $\text{pK}_2 = 5.5$).

Considering the resolution, sensitivity and analysis time, the eluent selected was 1 mM potassium hydrogenphthalate at pH 5.5. The appearance of the system peak under these conditions can be avoided by injecting the sample dissolved in the mobile phase. The values of k' and resolution under these conditions are given in Table I. It can be seen that resolution was always higher than 1.4.

Naphthalenesulphonate eluents have recently been proposed for the determination of anions with indirect photometric detection [16–20]. The advantages of these eluents include their stability, the use of longer detection wavelengths, non-dependence of the elution strength on pH, absence of system peaks and lower detection

TABLE I

COMPARISON OF RESOLUTIONS AND CAPACITY FACTORS OBTAINED WITH DIFFERENT ELUENTS

Anion	Borate–gluconate ^a		Hydrogenphthalate ^b		Naphthalenesulphonate ^c		Naphthalenedisulphonate ^d	
	<i>k'</i>	<i>R_s</i>	<i>k'</i>	<i>R_s</i>	<i>k'</i>	<i>R_s</i>	<i>k'</i>	<i>R_s</i>
H ₂ PO ₄ ⁻	–	–	6.26	1.82	–	–	–	–
Cl ⁻	6.44	1.65	12.26	2.21	29.50	1.00	4.75	0.80
NO ₂ ⁻	9.33	1.59	18.26	1.46	36.50	1.17	6.00	1.33
Br ⁻	12.69	1.52	23.50	1.85	45.00	0.64	7.00	4.36
NO ₃ ⁻	16.40	1.53	31.26	–	52.00	0.00	9.00	2.80
HPO ₄ ²⁻	23.30	3.45	–	1.85	52.90	–	21.00	3.52
SO ₄ ²⁻	35.21	–	56.00	–	–	–	31.50	–

^a Borate–gluconate, 1.3 mM, pH 8.5.^b Hydrogenphthalate, 1.0 mM, pH 5.5.^c Naphthalenesulphonate, 0.3 mM, pH 7.^d Naphthalenedisulphonate, 0.1 mM, pH 10.

limits. Their use for the determination of several anions has been proposed but no information is available about their applicability to the determination of phosphate.

Using 0.3 mM 2-naphthalenesulphonate–acetonitrile (90:10) as eluent, phosphate co-eluted with nitrate; the capacity factor for phosphate varied because a non-buffered eluent was used at pH 6.8 (near p*K* = 7.2 for the dihydrogenphosphate ion). Working at lower pH (4) or using 0.3 mM 2-naphthalenesulphonic acid–acetonitrile (90:10) did not help as a system peak appeared that co-eluted with phosphate. Consequently, the determination of phosphate ion was impossible.

The other eluent tested was 1,5-naphthalenesulphonate. The capacity factor for phosphate also varied because a non-buffered mobile phase was used. The behaviour of this eluent at pH 10, at which the monohydrogenphosphate species was predominant, was studied. The chromatogram obtained for the common ions, including phosphate and sulphate, is given in Fig. 2. Complete separation was not achieved but this eluent can be used for the determination of

nitrate, phosphate and sulphate. Capacity factors and resolution for these conditions are given in Table I.

The detection limits were calculated as a response higher than twice the standard deviation of the background noise. Table II gives the values obtained with conductimetric and direct or indirect photometric detection using borate–gluconate, methanesulphonic acid, hydrogenphthalate and 1,5-naphthalenesulphonate eluents. Although nitrate had a low detection limit using the 1,5-naphthalenesulphonate eluent, the best result was obtained with direct photometric detection. The detection limits obtained with the 1,5-naphthalenesulphonate eluent are generally lower than those obtained using the other phases, and are in agreement with those previously reported for similar mobile phase concentrations [17,18,20]. The values obtained for phosphate by indirect photometric detection are better than those using conductimetric detection, which may be due to the elution of the dihydrogenphosphate with a low retention time when phthalate is used as eluent or to the higher molar absorptivity and lower

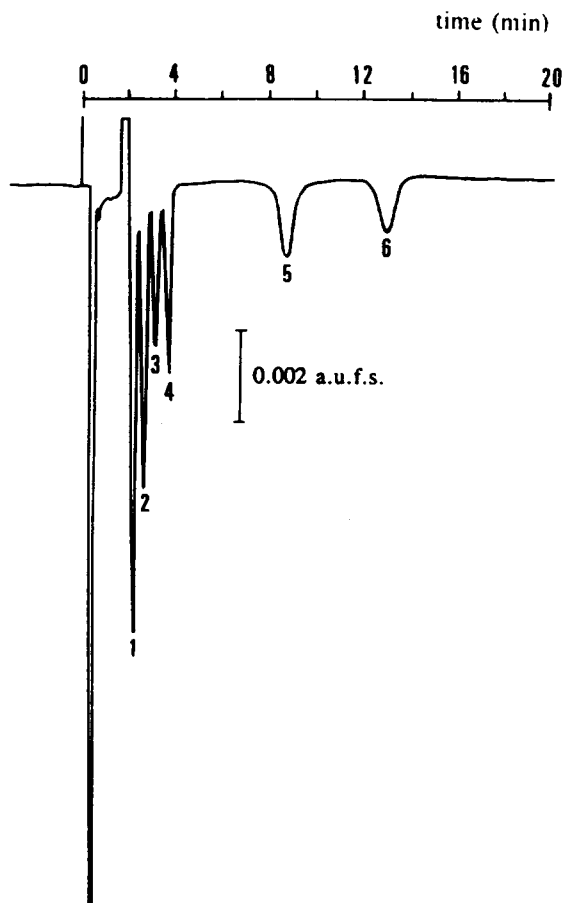


Fig. 2. Separation of a standard mixture of inorganic anions. Peaks: 1 = Cl^- ; 2 = NO_2^- ; 3 = Br^- ; 4 = NO_3^- ; 5 = HPO_4^{2-} ; 6 = SO_4^{2-} . Column, Waters IC Pak A; eluent, 0.1 mM 1,5-naphthalenedisulphonate–acetonitrile (90:10); flow-rate, 1.2 ml/min; indirect UV detection at 285 nm; sample, 100 μl , 1 mg/l.

baseline noise of the 1,5-naphthalenesulphonate. Indirect photometry using phthalate or 1,5-naphthalenesulphonate was the most sensitive detection method for the determination of phosphate.

Calibration for the anions was carried out in each of the solvents with concentrations in the range 0.5–20 mg/l. Peak area was used as the response. The correlation coefficients ranged from 0.9989 to 0.9999 for all analytes.

Ten replicate determinations of 1 mg/l of each anion was carried out under the optimum conditions for each mobile phase to determine the reproducibility. The relative standard deviations

(R.S.D.) of retention times and peak areas were 0.4–1.0% and 0.6–2.0%, respectively, when borate–gluconate or hydrogenphthalate was used. For the naphthalenesulphonate eluents higher R.S.D.s were obtained (0.9–3.0%).

Removal of sulphate using ion-exchange resins in Ba^{2+} form

There are some references to the use of ion-exchange resins in the Ba^{2+} form for the removal of sulphate in samples with high levels of this anion [10,11] but few of them give data about the recovery of phosphate; only Henderson *et al.* [10] reported recoveries of 96.5% using phosphate solutions of 30 mg/l.

In this study two reagents were used for the preparation of cation-exchange resin in the Ba^{2+} form: barium chloride and barium acetate. The results obtained using a sample of 100 mg/l of sulphate and 10 mg/l of phosphate were similar and the reagent was chosen depending on the anions to be determined in the sample.

The results obtained for the removal of sulphate and the recovery of phosphate using ion-exchange resins in the barium form in the column mode for different sulphate-to-phosphate concentration ratios are given in Table III. The amount of resin used in each instance was calculated taking into account the concentration of sulphate in the sample. The removal of sulphate was high for low concentration ratios up to a value of 100; when the amount of sulphate increased from 1000 to 5000 mg/l, a large decrease in sulphate removal was observed (recovery 17%). These results could not be improved using large columns (12 g) and may be explained in terms of the kinetics of the column; the flow in the column was too fast to allow effective retention. The recoveries obtained for the phosphate ion was not sufficiently high (see Table III) but the results were reproducible.

To optimize the elimination of sulphate in samples with high levels of this anion, a batch method with the barium ion-exchange resin was used. The amount of resin and the contact time for samples with a sulphate-to-phosphate ratio of 5000:10 (mg/l) were studied and the results are given in Table IV. An increase in the amount of resin gave a better elimination of sulphate, but

TABLE II

COMPARISON OF DETECTION LIMITS WITH CONDUCTIMETRIC AND DIRECT OR INDIRECT PHOTOMETRIC DETECTION

Compound	Detection limit (ng)			
	Conductimetric detection	Direct photometric detection	Indirect photometric detection	
			Phthalate	Naphthalenedisulphonate
Cl ⁻	0.5	–	0.5	–
NO ₂ ⁻	1.0	–	1.5	–
Br ⁻	2.5	–	5.0	–
NO ₃ ⁻	2.5	0.1	5.0	0.5
HPO ₄ ²⁻	5.0	–	0.9 ^a	1.0
SO ₄ ²⁻	2.5	–	5.0	1.0

^a As H₂PO₄⁻.

low recoveries of phosphate were observed for masses above 3 g, probably owing to the coprecipitation of this anion in the barium resin. Moreover, the recovery of phosphate increased with a decrease in the contact time. Therefore, we propose a batch procedure using 3 g of resin, leaving it to stand for 8 h to ensure the elimination of sulphate in samples in which the sulphate-to-phosphate ratio is 500 or higher (calculated as mg/l). The elimination of sulphate in this instance was 97.5% (R.S.D. 1.3%) and the recovery of phosphate was 51.5% (R.S.D. 14.2%).

One of the most versatile means of sample clean-up is the use of commercial disposable cartridges. We studied the behaviour of two

different commercial cartridges with different amounts of resin, Maxi-Clean Ba²⁺ and Maxi-Clean Ba²⁺ Plus with 1 and 3 g of resin, respectively. The results obtained are given in Table V. For samples with a sulphate-to-phosphate ratio of 100:10 (mg/l) recoveries of 55% were obtained, but for the other samples, which contained higher concentrations of sulphate, only the Maxi-Clean Ba²⁺ Plus cartridge could be used and the recovery of phosphate was lower than those obtained with the columns prepared in our laboratory. This illustrates one of the most important drawbacks of the method, *i.e.*, that the amount of resin must be adjusted according to the sample composition.

TABLE III

RECOVERIES OF PHOSPHATE WITH Ba²⁺ ION-EXCHANGE RESIN IN COLUMN MODE (*n* = 5)

SO ₄ ²⁻ :PO ₄ ³⁻ (mg/l)	Resin (g)	SO ₄ ²⁻		PO ₄ ³⁻	
		Average elimination (%)	R.S.D. (%)	Average recovery (%)	R.S.D. (%)
100:10	0.1	90.70	2.39	73.20	2.95
500:10	0.4	98.84	0.87	48.92	4.80
1000:10	1.5	99.69	0.08	49.67	0.91
5000:10	4.0	17.50	–	–	–
	12.0	15.90	–	–	–

TABLE IV

RECOVERIES OF PHOSPHATE WITH Ba^{2+} ION-EXCHANGE RESIN IN BATCH MODE ($n = 5$) FOR $\text{SO}_4^{2-}:\text{PO}_4^{3-} = 5000:10$ (mg/l)

Resin (g)	Contact time (h)	SO_4^{2-} elimination (%)	PO_4^{3-} recovery (%)
1.0	20	37.3	N.D. ^a
2.0	20	57.1	N.D.
2.5	48	99.9	1.5
2.5	20	99.6	15.0
2.5	14	86.0	34.3
2.5	10	81.0	37.5
3.0	8	97.5	51.5
3.5	4	95.0	19.0

^a N.D. = Not determined.

Analysis of saline sediments

In order to examine the suitability of the method for the determination of nitrate and phosphate in highly saline samples, several kinds of sediments from a saline circuit with calcite and gypsum domains were analysed. Chloride and nitrate were determined in the water-soluble fraction and their values ranged from 36.4 to 41.2 mg/g for chloride and from 0.20 to 0.50 mg/g for NO_3^- . Sulphate and phosphate were determined in the solution obtained by extraction of the sample with 1 M HCl and elimination of chloride using an ion-exchange resin in the Ag^+ form. Their values ranged from 0.07 to 0.22 mg/g for phosphate and from 12.40 to 465.40

mg/g for sulphate. Fig. 3A shows the chromatogram (conductimetric detection) for a sample with a low level of sulphate, where direct determination of nitrate and phosphate was possible.

Figs. 3B and 4A show the chromatograms (conductimetric and indirect UV detection) of a sample with high level of sulphate where nitrate and phosphate were not detected. In this instance elimination of sulphate was needed. In Fig. 4B the chromatogram obtained after elimination using the Ba^{2+} ion-exchange resin in the batch mode is shown.

CONCLUSIONS

The use of various eluents in ion chromatography with conductimetric or indirect UV detection for the determination of phosphate was tested. Low detection limits were obtained using indirect UV detection with phthalate or 1,5-naphthalenesulphonate eluents.

The results obtained for the recovery of phosphate using barium ion-exchange resins indicate that the procedure can be used for the determination of phosphate in samples with a large excess of sulphate. The elimination of the major interfering anions using anion-exchange resins and determination by ion chromatography is a precise and sensitive method for the determination of anions in saline samples and may therefore have advantages over conventional colorimetric methods.

TABLE V

RECOVERIES OF PHOSPHATE WITH A COMMERCIAL Ba^{2+} CARTRIDGES ($n = 5$)

$\text{SO}_4^{2-}:\text{PO}_4^{3-}$ (mg/l)	Maxi-Clean Ba^{2+}				Maxi-Clean Ba^{2+} Plus			
	SO_4^{2-}		PO_4^{3-}		SO_4^{2-}		PO_4^{3-}	
	Average elimination (%)	R.S.D. (%)	Average recovery (%)	R.S.D. (%)	Average elimination (%)	R.S.D. (%)	Average recovery (%)	R.S.D. (%)
100:10	94.5	1.4	55.0	5.2	95.4	1.6	54.2	8.9
500:10	34.2	2.3	—	—	95.9	0.5	11.9	19.2
1000:10	—	—	—	—	94.4	1.1	3.9	20.7
5000:10	—	—	—	—	35.2	1.5	—	—

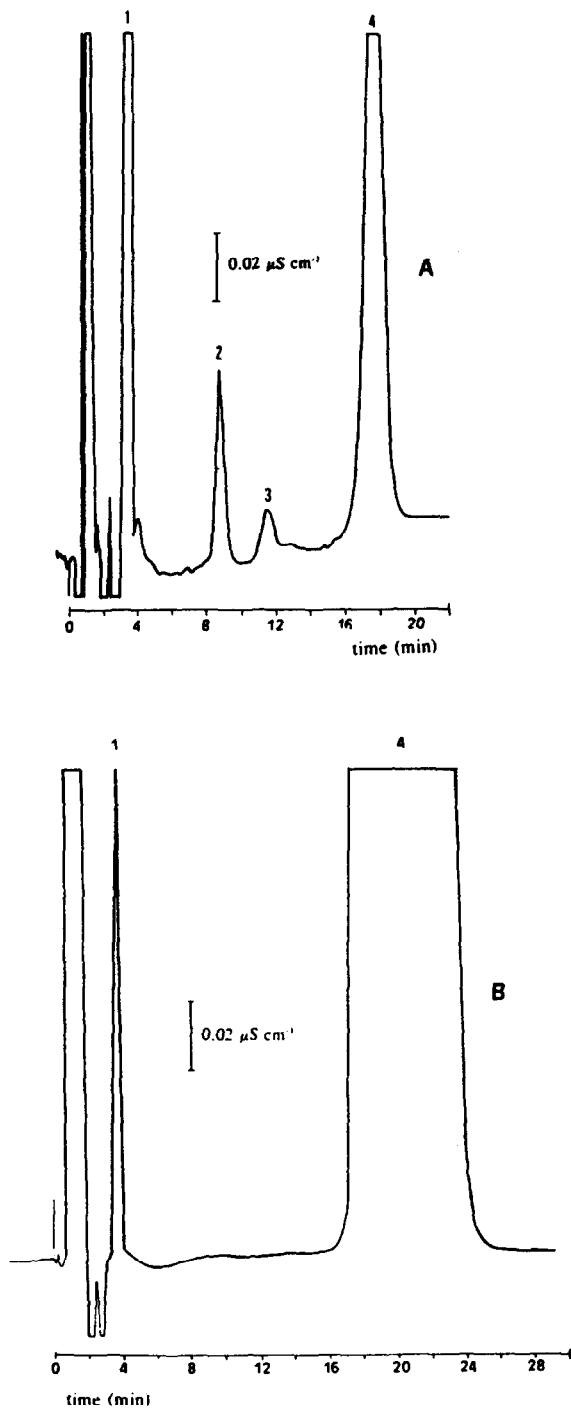


Fig. 3. Chromatograms of saline sediments. (A) Sample with a low level of sulphate (12.4 mg/g); (B) sample with a high level of sulphate (465.4 mg/g). Peaks: 1 = Cl^- ; 2 = NO_3^- ; 3 = HPO_4^{2-} ; 4 = SO_4^{2-} . Column, Waters IC Pak A; eluent, 1.3 mM borate-gluconate (pH 8.5); flowrate, 1 ml/min; conductimetric detection.

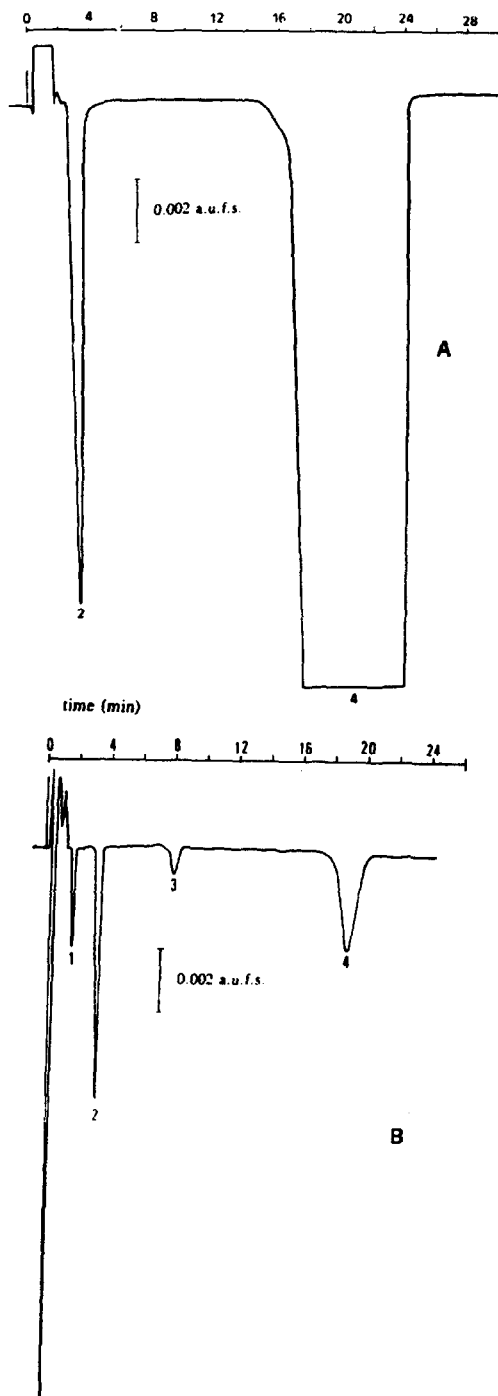


Fig. 4. Chromatograms of a saline sediment with a high level of sulphate (465.4 mg/g). (A) Without sulphate elimination; (B) after sulphate elimination. Peaks: 1 = H_2PO_4^- ; 2 = Cl^- ; 3 = NO_3^- ; 4 = SO_4^{2-} . Column, Waters IC Pak A; mobile phase, 1 mM potassium hydrogenphthalate (pH 5.5); flowrate, 1 ml/min; indirect UV detection at 285 nm.

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