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Column-switching techniques in the analysis of phosphate by ion chromatography☆

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Abstract

A comparative study of ion chromatography systems for the analysis of phosphate in samples with high levels of sulphate has been performed. Two low-capacity ion-exchange columns, a high-capacity column and switching systems with direct transfer and with loop transfer have been studied. A high-capacity column permits the determination of phosphate in samples with sulphate-to-phosphate ratio of 5000:10 (mg/l), but at this sulphate level the detection limit for phosphate was relatively high (200 ng). For the column-switching systems, switching time and phosphate detection limits have been studied. A low detection limit (50 ng) was obtained using direct-transfer column switching at sulphate concentrations of 4000 mg/l. A similar detection limit was obtained using a loop-transfer column-switching system with a high-capacity column as a primary column for levels of sulphate of 5000 mg/l. Their applicability for the analysis of water samples is demonstrated.

1. Introduction

Ion chromatography (IC) is an effective technique to determine trace anions in a variety of samples but its application to sample matrices of extreme ionic strength shows some difficulties. Anions at relatively low concentrations (100–1000 mg/l) often cause overload and peaks become broad because of the low capacity of the ion exchanger used (less than 0.1 mequiv./g). Moreover, high concentrations of ionic compounds in this kind of sample induce retention time variability, loss of chromatographic efficiency and resolution, decrease in the column lifetime and increase in the background of the conductivity detector.

Several procedures have been suggested to overcome the adverse effects of matrix ions. The concentration of these ions in the sample can be reduced prior to the analysis by using a suitable precolumn filled with an ion-exchange resin [1–5], hollow-fibre ion-exchange membranes [6,7], dialysis through membranes [8,9] or electrodialysis [10–13]. The use of the interfering ion as the eluent [14,15] and the use of gradient IC [16] have also been proposed for samples containing high ratios of ion concentrations.

Few methods are proposed for the elimination of sulphate in highly saline samples but the use of precolumns with ion-exchange resins in the barium form is recommended [3–5]; this pro-

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cedure is time consuming and the recoveries of phosphate are low [5].

Commercial columns with moderate capacity, because of their length, can give better resolutions and may be used in the analysis of samples with anions at different concentrations. We studied the applicability of one of these columns to the analysis of phosphate in samples with high levels of sulphate. The highest sulphate-to-phosphate ratio that allows the determination of phosphate was established and the detection limit for phosphate at different ratios was calculated.

On the other hand, on-line multidimensional chromatography permits complex samples to be broken down into manageable portions, resulting in improved speed, precision and chromatographic resolution. Column switching involves the cleanup and separation of multicomponent mixtures by on-line selective transfer of a fraction from one chromatographic column to one or more secondary columns for additional separation. These techniques have been used for the elimination of chloride from different samples, such as concentrated inorganic acids, water and brine [17–20], of weak organic acid anions in water [21] or large amounts of interferent compounds in the determination of sulphite in a variety of samples [22,23]. Few applications of these methods have been described for the elimination of sulphate in saline samples [21,24], and none of them has been used for the analysis of phosphate. In this study column-switching techniques with direct or with loop transfer for the elimination of sulphate in saline samples before phosphate determination are described. Column-switching time and detection limits for samples with different sulphate-to-phosphate ratios are established.

2. Experimental

2.1. Instruments

The liquid chromatograph consisted of an LKB (Bromma, Sweden) Model 2150 pump, a Rheodyne (Cotati, CA, USA) Model 7125 valve (100-μl loop), a Rheodyne Model 7000 valve and a Metrohm (Herisau, Switzerland) Model 690 conductivity detector. A data processor, Chromatopac C-R3A (Shimadzu, Kyoto, Japan), was used. Two different anion-exchange analytical columns, both based on aminated polymethacrylate resin (exchange capacity 30 μequiv./g), were used. These were a Waters (Milford, MA, USA) IC Pak A (50 × 4.6 mm I.D.; particle size 10 μm) and a high-capacity Waters IC Pak A HC (150 × 4.6 mm I.D.; particle size 10 μm).

2.2. 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. For samples with high levels of sulphate a 20 000 mg/l stock solution of this anion was prepared and used for further dilutions. Water was purified using a Culligan system and filtered through a 0.45-μm membrane.

Sodium gluconate (97%), boric acid, glycerine (87%) and acetonitrile were obtained from Merck (Darmstadt, Germany). Sodium tetraborate was obtained from Carlo Erba (Milan, Italy).

2.3. Chromatographic conditions

Non-suppressed IC with conductimetric detection using borate–gluconate [1.3 m*M* tetraborate, 5.8 m*M* boric acid, 1.3 m*M* gluconate, 5 g/l glycerine (pH 8.5) and 120 ml/l acetonitrile] at 1 ml/min with a Waters IC Pak A and two Waters IC Pak A on-line, and at 2 ml/min with a Waters IC Pak A HC was used for the determination of phosphate. All eluents were prepared daily, filtered and degassed.

2.4. Column-switching systems

The flow diagram of the column-switching system A, direct transfer, is shown in Fig. 1. This system was equipped with two Waters IC Pak A columns on-line. The primary mobile phase entered the valve (IN) and flushed the primary

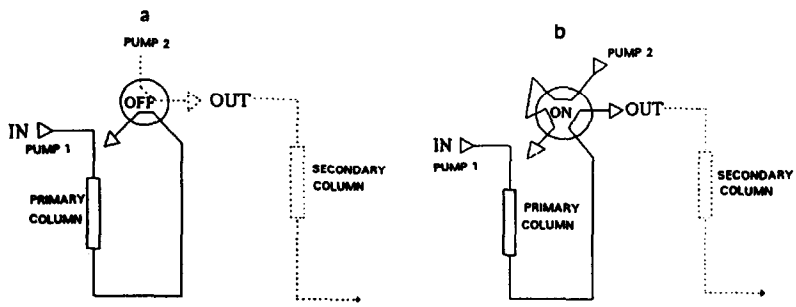


Fig. 1. Column-switching system A. (a) Elution of primary column. (b) Transfer on to the secondary column with primary eluent.

column (Fig. 1a). When the analyte eluted, the switching valve was rotated into the transfer position (ON) (Fig. 1b). The separated analyte fraction was directed through the OUT port to the secondary column; then the valve was rotated back and the secondary mobile phase (PUMP 2) started to elute the analyte from the secondary column.

The column-switching system B was the same as system A, except that it was equipped with a sample loop (2 ml) between the two columns and the primary was a high-capacity column, IC Pak A HC and the secondary an IC Pak A. The primary and secondary columns were not connected on-line during the transfer period to avoid excessive pressure on the columns during the transfer. The analyte effluent from the primary column was collected in a loop and reinjected into the secondary column.

3. Results and discussion

Borate–gluconate is a mobile phase that permits sensitive detection and efficient separation in IC using aminated polymethacrylate columns. To examine the effect of high levels of sulphate on the resolution between sulphate and phosphate using borate–gluconate as mobile phase, samples with 10 mg/l of phosphate and different concentrations of sulphate from 100 to 5000 mg/l were analyzed.

A low-capacity (5 cm), two on-line low-capacity columns and a high-capacity column (15 cm) were used. In Table 1 data for the separation of sulphate and phosphate with different columns are given. For sulphate concentration below 500 mg/l baseline resolution between phosphate and sulphate was always attained. In Fig. 2 the chromatograms obtained with a low-capacity column for samples with sulphate-to-phosphate ratios of 100:10 (mg/l) and 500:10 (mg/l) are shown. An increase in the amount of sulphate gave worse separation and, at 1000 mg/l of sulphate, no separation at all was observed due to the overloading of the sample anions on a low-capacity ion-exchange resin. Although an improvement in resolution between phosphate and sulphate can be obtained at pH lower than 8.5 a decrease in the eluting strength of the eluent occurred, giving higher retention times and worse detection limits. An increase in the column capacity may give better results. For two columns connected on-line enough resolution can be obtained until ratios 4000:10 as can be seen in Fig. 3A. At higher sulphate concentration the phosphate and sulphate peaks co-eluted.

At higher sulphate concentration, 5000 mg/l, only a high-capacity column allowed the separation of phosphate (Fig. 3B), although a distortion of the peaks occurred due to the high level of sulphate. It must be pointed out that the performance of the analysis was strongly dependent on the behaviour of the column, retention time and resolution decreased considerably after 100 injections at this sulphate concentration.

Table 1 shows that the retention time of the phosphate decreased with an increase in the amount of sulphate. This decrease can be explained since sulphate is a stronger eluent than borate–gluconate. With a large sulphate loading,

Table 1
Separation of sulphate and phosphate in anion-exchange columns

SO_4^{2-}:PO_4^{3-} (mg/l)	Columns					
	Low-capacity column		Two low-capacity columns		High-capacity column	
	t_R (min)	Δt (min)	t_R (min)	Δt (min)	t_R (min)	Δt (min)
100:10	13.2	4.3	24.1	8.1	22.6	8.6
500:10	12.1	2.1	23.8	6.1	22.5	6.8
1000:10	Coelution		23.2	5.0	22.1	5.8
2000:10	Coelution		22.8	4.2	21.8	4.1
2500:10	Coelution		22.6	3.5	21.3	3.6
3000:10	Coelution		21.9	2.7	20.9	3.0
3500:10	Coelution		21.5	2.1	20.5	2.6
4000:10	Coelution		21.2	1.6	20.3	2.3
4500:10	Coelution		Coelution		20.1	2.0
5000:10	Coelution		Coelution		19.7	1.9

it can be assumed that the borate–gluconate eluent ion is partially replaced by sulphate ion, which leads to a decrease in the retention times.

3.1. Column-switching procedures

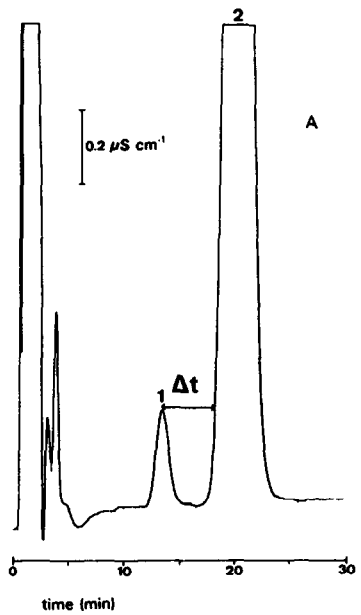
For the analysis of phosphate in a highly concentrated matrix of sulphate two column-switching systems were studied. System A (see Fig. 1) used a direct-transfer technique, and system B a loop-transfer one.

In both techniques, the system was initially assembled with only the primary column in order to determine the column-switching time interval, which is the time between the onset of the analytical peak and its complete elution. For high amounts of sulphate, since the primary column was overload, the column-switching time for each sample must be determined using the coupled system. For example in Fig. 4 the results obtained when switching from 10 to 13 min, from 6 to 8 min and from 3 to 6 min for a sample with a sulphate-to-phosphate ratio of 5000:10 (mg/l) are given, the highest recoveries (71.3%) were obtained when switching from 6 to 8 min. Samples with less sulphate gave higher recoveries of phosphate; for example for samples with a sulphate-to-phosphate ratio of 4000:10 the recovery was 92.5%.

Calibration for phosphate in samples with different levels of sulphate was carried out using the standard addition method; peak area was used as the response. The correlation data show good linearity for phosphate; for example for samples with 5000 mg/l of sulphate the correlation coefficient for phosphate (5–25 mg/l) was 0.9989.

To determine the reproducibility of the technique eight replicate determinations of 10 mg/l of phosphate were carried out for the optimum column-switching time. The relative standard deviation (R.S.D.) of peak areas was 1.5%.

Detection limits for phosphate were calculated as a response higher than three times the standard deviation of the background noise. The values obtained using a low-capacity, two on-line low-capacity columns, a high-capacity column and the column-switching systems are given in Table 2. A low detection limit (5 ng) was obtained with a low-capacity column for samples without sulphate, but there was an increase in the detection limit when columns with higher capacity were used or when the sulphate content was raised. This increase was more pronounced at high levels of sulphate and may be related to a distortion in the phosphate peak and in the baseline. In the column-switching system with direct transfer, phosphate detection limits re-



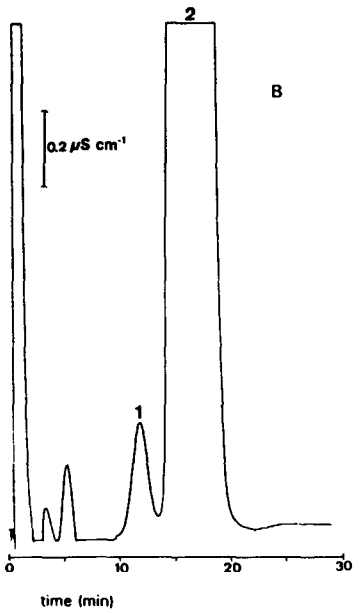
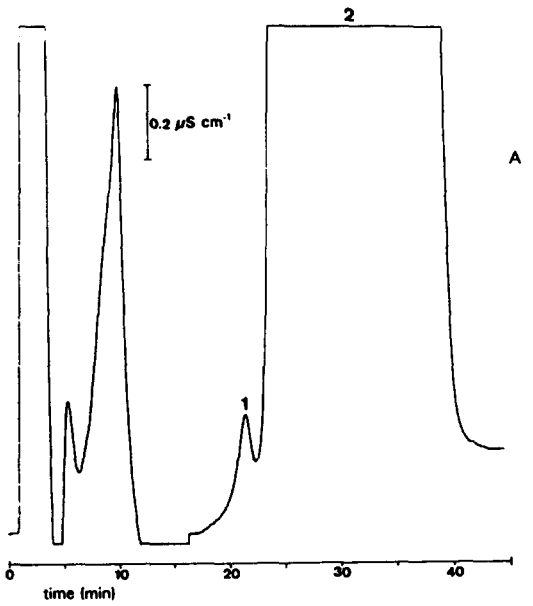


Fig. 2. Chromatograms of the separation of phosphate and sulphate with a low-capacity column (1 ml/min). (A) Sulphate-to-phosphate ratio 100:10 (mg/l), (B) sulphate-to-phosphate ratio 500:10 (mg/l). Peaks: $1 = HPO_4^{2-}$; $2 = SO_4^{2-}$.



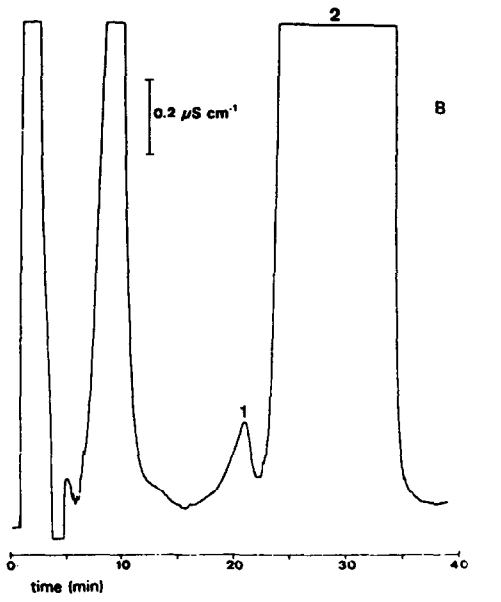


Fig. 3. Chromatograms of the separation of phosphate and sulphate. (A) Two low-capacity columns on-line (1 ml/min), sulphate-to-phosphate ratio 4000:10 (mg/l); (B) high-capacity column (2 ml/min), sulphate-to-phosphate ratio 5000:10 (mg/l). Peaks: $1 = HPO_4^{2-}$; $2 = SO_4^{2-}$.

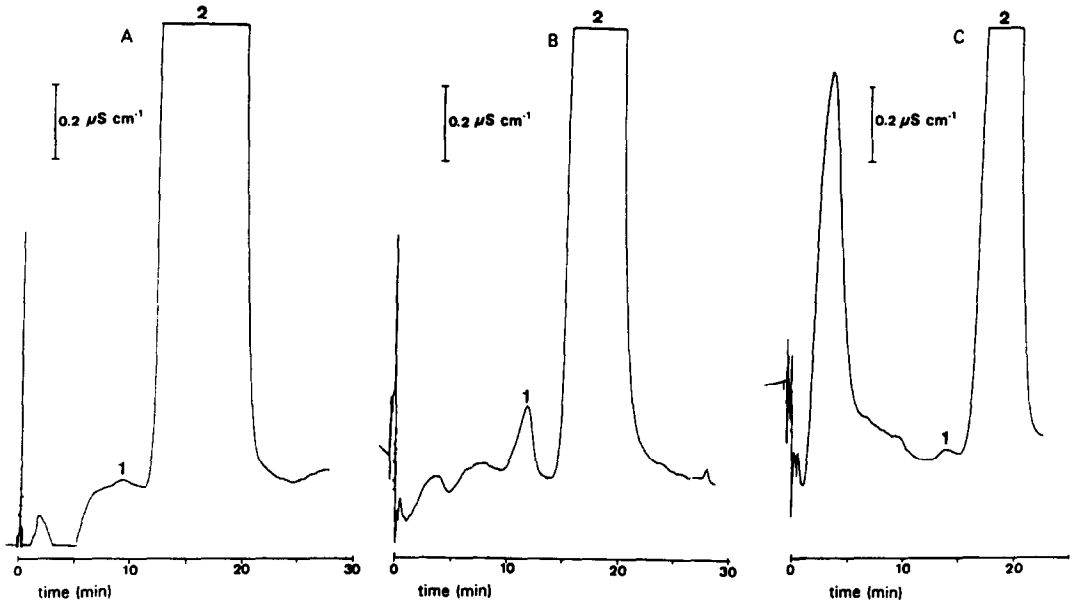


Fig. 4. Chromatograms of the optimization of column-switching time with direct transfer (system A). (A) Column-switching time from 10 to 13 min, (B) column-switching time from 6 to 8 min, (C) column-switching time from 3 to 6 min. Peaks: 1 = HPO_4^{2-}; 2 = SO_4^{2-}.

mained constant for sulphate concentrations between 100 and 1000 mg/l. This behaviour was due to the elimination of the sulphate ion. When the concentration of sulphate increased to 4000 mg/l a rise in the detection limit was observed but this was always lower than that obtained with the other systems. Using a column-switching system with loop transfer and a high-capacity column, higher detection limits for low levels of sulphate were observed related with a diffusion of the solute in the loop, which gives broad peaks. Detection limits were similar for all sulphate concentrations; so for samples with high levels of sulphate the best detection limits were obtained using the switching system. This can be explained due to the high capacity of the primary column, which prevents overloading, and as a result no sulphate enters in the secondary column.

The analysis time using column-switching techniques was 30 min, similar to the time needed for the analysis with a high-capacity column. The

Table 2
Detection limits obtained with different systems

System	Detection limit (ng)					
	SO_4^{2-} concentration (mg/l)					
	0	100	500	1000	4000	5000
Low-capacity column	5	8	35	–	–	–
Two low-capacity columns on-line	15	20	40	50	150	–
High-capacity column	25	35	50	60	80	200
Column switching direct transfer	15	20	20	20	50	100
Column switching loop transfer	35	35	40	40	40	50

reequilibration time before the injection of a second sample can be eliminated if the primary column is continuously flushed with the mobile phase.

To show the applicability of the method in samples with high levels of sulphate, column-switching system A was used for the analysis of synthetic samples with a sulphate-to-phosphate ratio of 5000:10 (mg/l) using the standard addition method; the R.S.D. was 3.4% ($n = 5$).

4. Conclusions

Different IC systems for the analysis of phosphate in samples with high excess of sulphate were compared. For sulphate-to-phosphate ratios lower than 500:10 (mg/l) low-capacity columns can be used. A high-capacity column or two low-capacity columns on-line are needed for samples with sulphate levels between 500 and 4000 mg/l. In samples with a high excess of sulphate, column-switching techniques give better results. Low detection limits for phosphate, at the ng level, in samples with high levels of sulphate, 4000–5000 mg/l, were obtained using column switching with direct or loop transfer. These procedures are reproducible, have high recoveries, are faster than other conventional off-line methods of elimination of sulphate and can be proposed for the analysis of phosphate in highly saline samples. Further applications of the technique are now being studied.

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