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Stationary phase for the determination of fluoride and other inorganic anions

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Abstract

A pellicular anion-exchange column was developed for the determination of inorganic anions including fluoride and oxyhalides such as chlorite, chlorate and bromate. Compared with conventional latex-agglomerated resins, the new anion exchanger allows the retention of fluoride well out of the water dip with elution of sulfate in less than 15 min using a carbonate–hydrogencarbonate eluent under isocratic conditions. Because the ethylvinylbenzene–divinylbenzene substrate is highly cross-linked, the new separator is solvent compatible, thus allowing the use of organic solvents to alter the selectivity of the separation, and also to remove organic contaminants from the column. The separation characteristics of this column are presented and various applications are discussed.

1. Introduction

Since the introduction of ion chromatography for the determination of inorganic anions in 1975 [1], the determination of fluoride has been a problem owing to its low affinity towards strongly basic anion exchangers [2–4]. To elute fluoride together with other common inorganic anions such as chloride, nitrate and sulfate within an acceptable time frame of less than 15 min, mixtures of sodium carbonate and sodium hydrogencarbonate are the most widely used eluents [5]. Another advantage of carbonate–hydrogencarbonate-based eluents is their compatibility with membrane-based suppressor systems, which are essential for the sensitive conductimetric detection of sample analytes. However, under these chromatographic conditions fluoride elutes very close to the system void volume, making determination at concentration levels of less than 100 μg/l difficult if not impossible owing to interference from the negative water dip. The water dip occurs when the injected water passes the conductivity cell, decreasing the background conductivity of carbonic acid formed in the suppressor by exchanging the eluent cations with hydronium ions.

There have been numerous attempts to circumvent this problem by sample pretreatment, by changing the eluent conditions or by tailoring the stationary phase design. An easy way to compensate for the negative dip is to add carbonate to the sample, matching the carbonate concentration in the mobile phase, thus making the negative dip invisible. However, this approach does not work with real samples such as mineral waters. If the carbonate concentration in the sample is higher than the total carbonate

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concentration in the mobile phase, a positive signal that is almost indistinguishable from the fluoride peak is obtained within the void volume of the separator column. Diluting the sample with deionized water does not solve this problem because even small amounts of carbonate in the sample lead to a significant decrease in the fluoride peak height [6]. Another problem for the verification of fluoride, especially in environmental samples, is monocarboxylic acids. As many of these acids co-elute with or are only partly resolved from fluoride, interpretation of the signals near the void volume is extremely difficult.

The exact determination of fluoride is possible if the advantage of the simultaneous determination of other mineral acids is eliminated and if the chromatographic conditions are changed so that fluoride is separated from the carbonate–hydrogencarbonate travelling with the mobile phase. An increase in fluoride retention can be achieved by using an eluent of lower eluting power such as sodium tetraborate. This method has only limited applicability because sulfate has a much longer retention time under these conditions, interfering with subsequent analyses. Alternatively, a gradient technique with sodium hydroxide as the eluent can be employed. Starting with very dilute NaOH solution, fluoride and various other monocarboxylic acids can be separated, while the final NaOH concentration suffices to elute other inorganic and organic anions of higher valencies.

IonPac AS10 was the first anion exchanger effectively to address the resolution of fluoride from the system void volume by combining a high ion-exchange capacity with a relatively weak eluent. The main drawback to the use of this column for general ion chromatographic applications is that the elution times for bromide and nitrate exceed 40 min under standard conditions. These analysis times are significantly longer than what is required of ion chromatography in a water analysis laboratory. We also evaluated a commercially available polymeric quaternary ammonium compound (quat)-coated resin from another source as it allows the resolution of fluoride from the system void volume with a standard carbonate eluent. As shown in Fig. 1, the separation of fluoride compares well with that obtained with ion-pair chromatography with the advantage of a much shorter analysis time. However, during the evaluation of this column we discovered that the polymeric quat-coated resin permanently loses its capacity following treatment with organic solvents (Fig. 2). Solvent levels as low as 10% caused significant decreases in column capacity. Recognizing the importance of solvents in cleaning contaminated ion-exchange materials and in altering ion-exchange selectivity, we began a project to develop a new solvent-compatible ion-exchange material with which fluoride is resolved from the system void volume and oxyhalides are separated from other mineral acids in the same run under isocratic conditions.

Because of the high degree of hydration of the

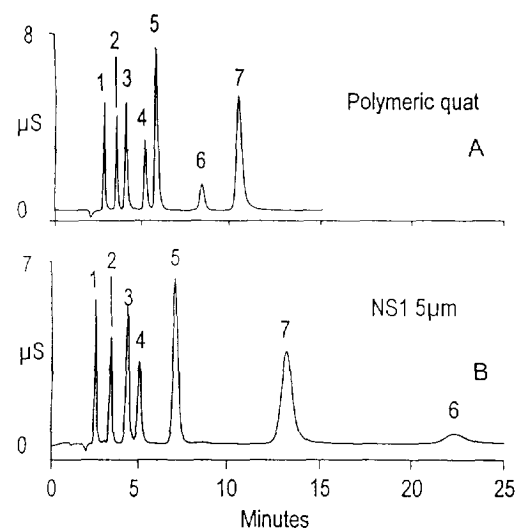

Fig. 1. Comparison of anion separations using ion-exchange chromatography on a polymeric quat-coated resin and ion-pair chromatography on highly cross-linked divinylbenzene. (A) Separator, polymeric quat-coated resin; eluent, 1.7 mmol/l sodium hydrogencarbonate–1.8 mmol/l sodium carbonate; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 25 µl. (B) Separator column, IonPac NS1 (5 µm); eluent, 2 mmol/l TBAOH + 1 mmol/l sodium carbonate–acetonitrile (90:10, v/v); flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume, 25 µl. Solute concentrations: (1) 3 mg/l fluoride; (2) 4 mg/l chloride; (3) 10 mg/l nitrite; (4) 10 mg/l bromide; (5) 20 mg/l nitrate; (6) 10 mg/l orthophosphate; (7) 20 mg/l sulfate.

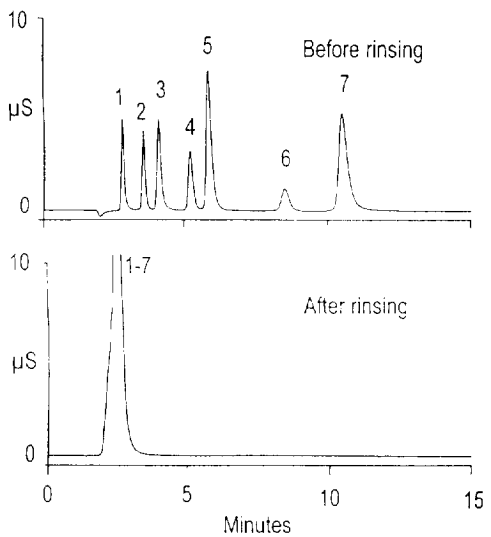

Fig. 2. Evaluation of a polymeric quat-coated resin for solvent resistance. Eluent, 1.7 mmol/l sodium hydrogencarbonate–1.8 mmol/l sodium carbonate; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 25 µl; solute concentrations as in Fig. 1. (A) Before rinsing with acetonitrile–water (90:10, v/v); (B) after a 30-min rinse with acetonitrile–water (90:10 v/v).

fluoride ion, it was necessary to generate a stationary phase with an extremely high water content. This can be accomplished by using very hydrophilic quaternary ion-exchange sites. However, fluoride is so highly hydrated that the only viable method of obtaining a reasonable fluoride retention is to produce an extremely low cross-linked latex. Using a cross-link level significantly under 1% allows the generation of polymers of very high water content needed for the effective retention of fluoride.

A key point in successful trace fluoride determination is that the eluent conductivity needs to be moderate. The higher the eluent conductivity, the greater is the void dip for any given column. Given the proximity of fluoride to the void dip, its absolute size needs to be minimized to allow maximum resolution of fluoride from the void dip. We therefore tried to develop a column that would work with as dilute an eluent as possible. We also determined that the higher the flow-rate, the faster the system void peak recovers to the baseline. Therefore, the column of choice should work at flow-rates above 1 ml/min. In order to obtain an acceptable capacity, given that a very low cross-linked latex had to be employed, we had to use a superporous substrate such as that used in the IonPac AS10 column mentioned earlier. The surface area of standard microporous packing materials is inadequate to provide sufficient capacity with these low cross-linked latexes.

The work presented in this paper was focused on the chromatographic properties and the applicability of such a packing material. In order to study this new separation material, chromatographic parameters such as eluent composition, eluent concentration and flow-rate were varied.

2. Experimental

2.1. Apparatus

All experiments were carried out with a DX 500 ion chromatographic system (Dionex, Sunnyvale, CA, USA) consisting of a quaternary gradient pump (GP40), a chromatography module (LC20) and a conductivity detector (CD20). Eluents were degassed by using the built-in vacuum solvent degassing device.

Separations were performed on an IonPac AS12A anion exchanger. A guard column (IonPac AG12A) was used all times. Conductivity detection was carried out using an Anion Self Regenerating Suppressor (ASRS-1) in the recycle mode.

A PeakNet chromatography data system (Dionex) was used for instrument control and for data collection and processing.

2.2. Reagents

Ultrapure water (18 MΩ/cm resistivity at 25°C) used for the preparation of the eluents was obtained from a water purification system (SERAL, Ransbach-Baumbach, Germany). Sodium hydrogencarbonate and sodium carbonate (Fluka, Ulm, Germany) and sodium tetraborate (Merck, Darmstadt, Germany) were of analyti-

Table 1
Structural and physical properties of the IonPac AS12A separator

Parameter	Value
Column dimensions	200 mm × 4 mm I.D.
Particle diameter	9 μm
Substrate material	Macroporous polyethylvinylbenzene cross-linked with 55% divinylbenzene
Pore size	200 nm
Column capacity	52 μequiv.
Latex polymer	Vinylbenzyl chloride
Latex cross-linking	Very low (0.15%)
Latex diameter	140 nm
Functional group	Quaternary ammonium group
pH stability	0–14
Solvent compatibility	0–100%

cal-reagent grade. Acetonitrile (Chrom AR grade) was purchased from Promochem (Wesel, Germany).

Dilute working standards of all inorganic anions and organic acids under investigation were prepared daily from 1000 ppm stock standard solutions. All standard solutions were stored in polyethylene containers.

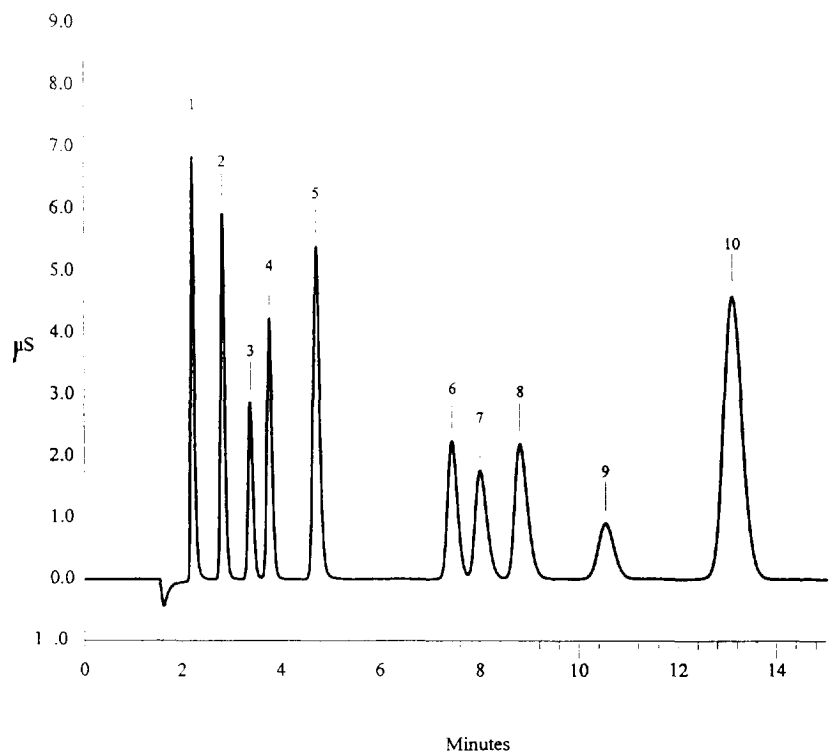

Fig. 3. Separation of common anions on IonPac AS12A. Eluent, 0.3 mmol/l sodium hydrogencarbonate–2.7 mmol/l sodium carbonate; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 25 μl. Solute concentrations: (1) 3 mg/l fluoride; (2) 10 mg/l chlorite; (3) 10 mg/l bromate; (4) 4 mg/l chloride; (5) 10 mg/l nitrite; (6) 10 mg/l bromide; (7) 10 mg/l chlorate; (8) 10 mg/l nitrate; (9) 10 mg/l orthophosphate; (10) 20 mg/l sulfate.

3. Results and discussion

The new anion exchanger for use as a stationary phase for the determination of fluoride and other inorganic anions has been commercialized under the trade-name IonPac AS12A. Its structural and physical properties are summarized in Table 1.

To accomplish all the objectives, we used a 0.15% cross-linked latex derived from vinylbenzyl chloride. The agglomeration of the latex was carried out on a superporous ethylvinylbenzene–divinylbenzene resin with a bead diameter of 9 μm, an average pore size of 200 nm and a specific surface area of approximately 15 m^2/g. The substrate was sulfonated under vigorous conditions to ensure that no unsulfonated surface existed on the substrate. This was necessary to avoid problems with the reversed-phase behaviour of anions such as bromide and nitrate. The ion-exchange capacity of this column is 52 μequiv. per column, or roughly double that of a conventional anion exchanger such as IonPac AS4A-SC. This doubling of capacity is remarkable considering that the water content of this latex is far higher than that of AS4A-SC. In latex-based ion-exchange materials, the ion-exchange capacity is inversely proportional to the latex water content because the water in the ion-exchange phase is essentially a diluent, occupying volume that would otherwise contain the ion-exchange polymer. Hence the superporous resin was necessary to compensate for the capacity by making use of a latex of high water content.

3.1. Water analysis

As with conventional latex-agglomerated anion exchangers such as the IonPac AS4A-SC and AS9-SC, generally used for water analysis applications, very simple eluents based on carbonate–hydrogencarbonate can be used to elute standard inorganic anions rapidly and efficiently

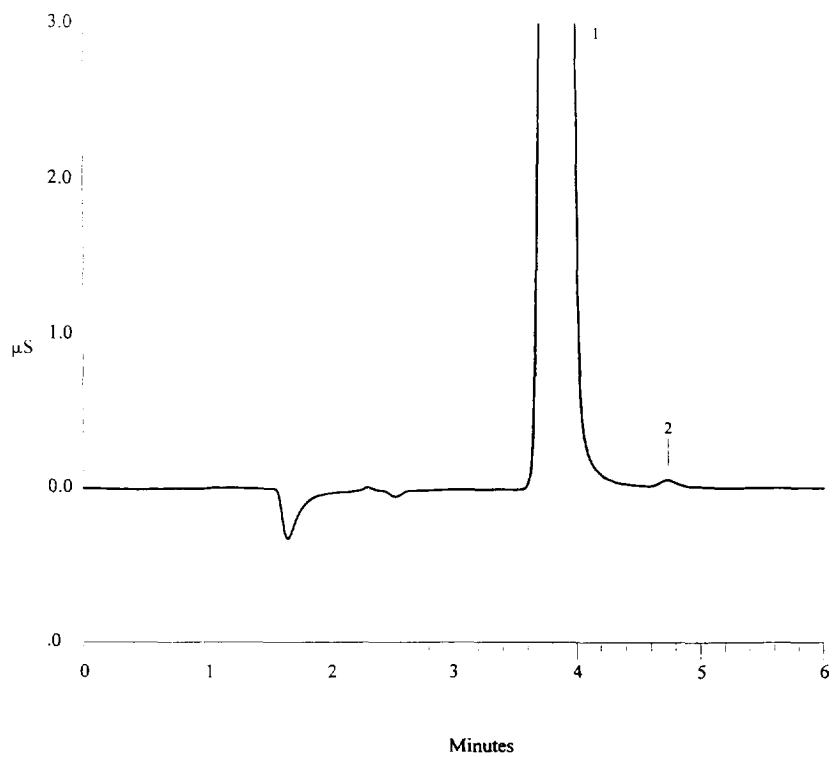

Fig. 4. Determination of nitrite in the presence of high chloride concentration. Separator, IonPac AS12A; chromatographic conditions as in Fig. 3. Solute concentrations: (1) 100 mg/l chloride; (2) 0.1 mg/l nitrite.

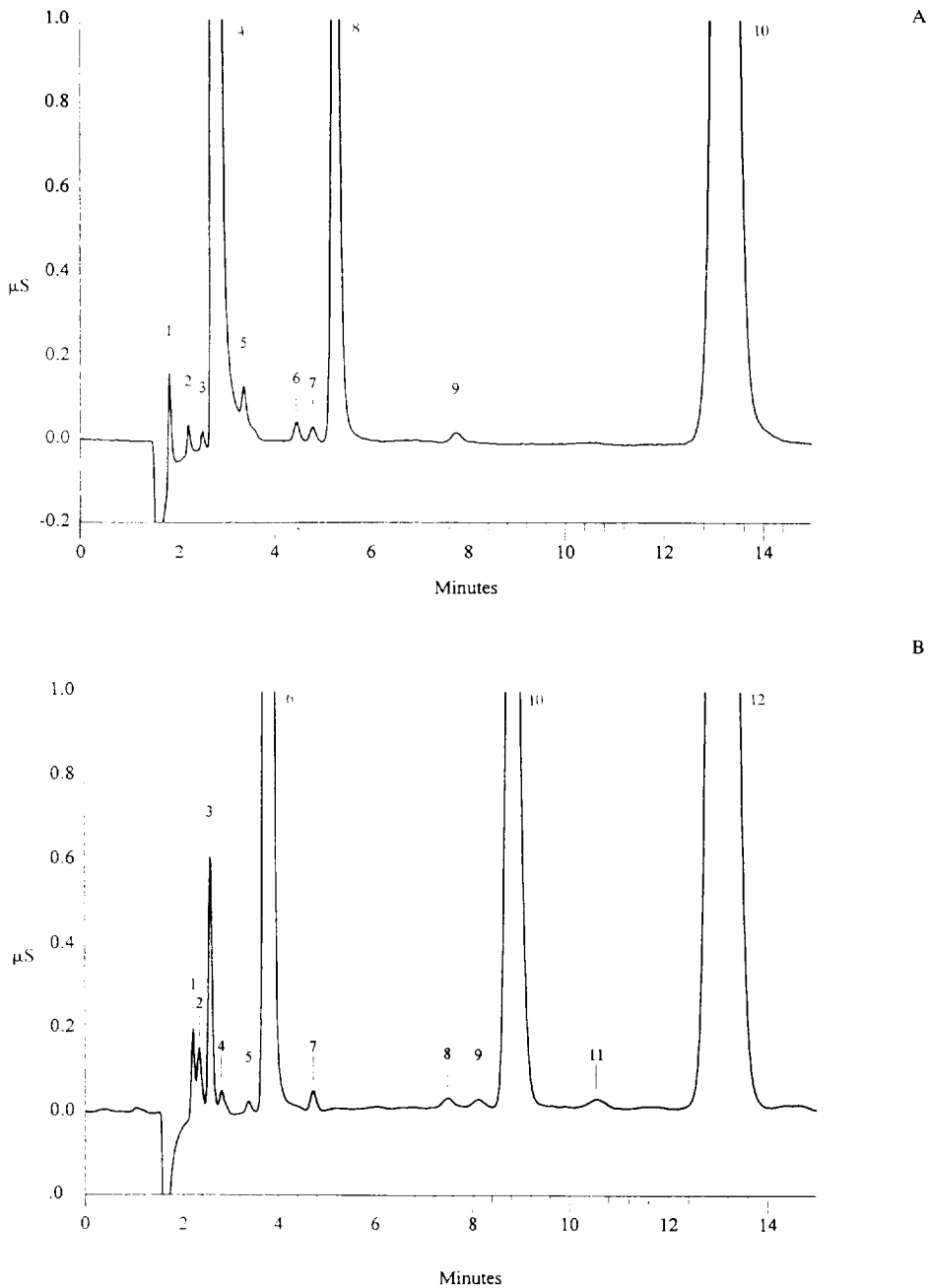

Fig. 5. Selectivity comparison of IonPac AS12A with the IonPac AS9-SC for the determination of common anions and disinfectant by-products in simulated drinking water. Separator column, (A) IonPac AS9-SC and (B) IonPac AS12A; eluent, (A) 1.7 mmol/l sodium hydrogencarbonate–1.8 mmol/l sodium carbonate and (B) 0.3 mmol/l sodium hydrogen-carbonate–2.7 mmol/l sodium carbonate; flow-rate, (A) 1 ml/min and (B) 1.5 ml/min; detection, suppressed conductivity; injection volume, 25 μl. Solute concentrations: (A) (1) 0.1 mg/l fluoride; (2) 0.1 mg/l chorite, (3) 0.1 mg/l bromate; (4) 20 mg/l chloride; (5) 0.1 mg/l nitrite; (6) 0.1 mg/l bromide; (7) 0.1 mg/l chlorate; (8) 5 mg/l nitrate; (9) 0.2 mg/l orthophosphate; (10) 20 mg/l sulfate; (B) (1) 0.1 mg/l fluoride; (2) 1 mg/l acetate; (3) 1 mg/l formate; (4) 0.1 mg/l chlorite; (5) 0.1 mg/l bromate; (6) 30 mg/l chloride; (7) 0.1 mg/l nitrite; (8) 0.1 mg/l bromide; (9) 0.1 mg/l chlorate; (10) 10 mg/l nitrate; (11) 0.2 mg/l orthophosphate; (12) 30 mg/l sulfate.

under isocratic conditions. Fig. 3 shows that fluoride is well resolved from the system void volume and separated to the baseline from other mineral acids and oxyhalides in less than 15 min, using a flow-rate of 1.5 ml/min and an eluent consisting of 2.7 mmol/l sodium carbonate and 0.3 mmol/l sodium hydrogencarbonate. Both the eluent composition and flow-rate were optimized for maximum resolution between all the analyte anions. It is remarkable that the large resolution between chloride and nitrite cannot be achieved by any other existing anion exchanger. This allows the separation of chloride and nitrite at large concentration differences, which previously was possible only with UV detection at 215 nm. Fig. 4 shows the separation of nitrite in presence of a 1000-fold excess of chloride employing suppressed conductivity detection.

Because of the increasing popularity of disinfecting water with ozone and chlorine dioxide, modern anion-exchange materials used for water analysis have to be capable of separating the most important disinfectant by-products such as chlorite, chlorate and bromate from other inorganic anions. Fig. 5 contrasts the new IonPac AS12A with the conventional acrylate-based IonPac AS9-SC anion exchanger, using simulated drinking water with more realistic concentrations of the disinfectant by-products as an example. As can be seen from these chromatograms, more than adequate resolution of both bromide and chlorate from nitrate can be achieved with both separators. However, the separation between fluoride, chlorite, bromate, chloride and nitrite on AS12A is clearly superior

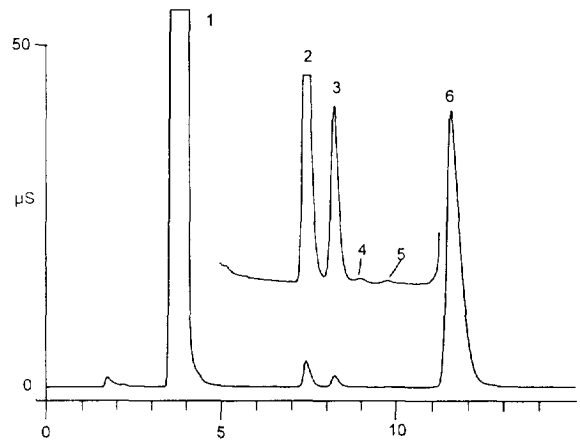

Fig. 7. Bath water analysis on an IonPac AS12A column. Chromatographic conditions as in Fig. 3; injection, 50 μl of a bath water sample with (1) 635 mg/l chloride, (2) 8.4 mg/l bromide, (3) 10 mg/l chlorate, (4) 0.04 mg/l nitrate, (5) 0.14 mg/l orthophosphate and (6) 105 mg/l sulfate.

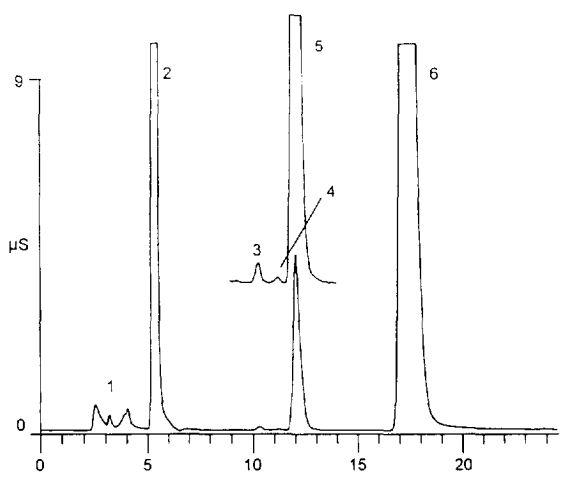

Fig. 6. Tap water analysis on an IonPac AS12A column. Chromatographic conditions as in Fig. 3; injection, 50 μl of a tap water sample with (1) 0.07 mg/l fluoride, (2) 58 mg/l chloride, (3) 0.17 mg/l bromide, (4) <0.10 mg/l chlorate, (5) 7.9 mg/l nitrate and (6) 75 mg/l sulfate.

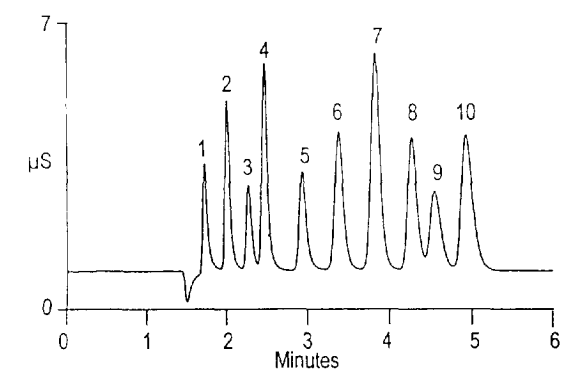

Fig. 8. Rapid separation of inorganic anions on an IonPac AS12A column. Eluent, 0.5 mmol/l sodium hydrogencarbonate–10.5 mmol/l sodium carbonate; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 10 μl. Solute concentrations: (1) 3 mg/l fluoride; (2) 20 mg/l chlorite; (3) 20 mg/l bromate; (4) 5 mg/l chloride; (5) 10 mg/l nitrite; (6) 30 mg/l orthophosphate; (7) 20 mg/l sulfate; (8) 20 mg/l bromide; (9) 20 mg/l chlorate; (10) 20 mg/l nitrate.

to that obtained with AS9-SC. Even short-chain fatty acids such as acetic acid, which co-elutes with fluoride on an AS9-SC column, can be partly separated from fluoride on an AS12A column under the given chromatographic conditions. In contrast, a polymeric quat-coated resin cannot be used for this purpose, as chlorite and chloride, nitrite and bromate and orthophosphate and chlorate co-elute, even under optimized chromatographic conditions. The only disadvantage of the AS12A column compared with the acrylate-based AS9-SC column is that polarizable anions such as iodide, thiocyanate and thiosulfate cannot be separated in the same run with mineral acids because they are highly retained.

Compared with the simulated drinking water shown in Fig. 5, the analysis of a real tap water sample renders more problems for determining anions with low affinities towards the stationary phase because of interferences in and around the system void volume. As shown in Fig. 6, fluoride can be separated from these interferences. However, the determination of chlorite, especially at trace levels, is interfered with by hydrogencarbonate present in this particular sample, thus displacing carbonate at the stationary phase. The displaced carbonate appears as a positive peak with a retention time similar to that of chlorite. The low chlorite concentration does not allow further dilution of the sample with deionized water, although this would remove the interference. Traces of chlorate, however, could be identified without any problems in this sample.

Because of its toxicity, chlorate is also a critical parameter in determining the water quality in swimming pools. The co-elution of nitrate and chlorate on conventional pellicular anion exchangers has often caused chlorate peaks to be misinterpretated as nitrate peaks. Fig. 7 shows a typical example of this kind of misinterpretation in the chromatogram of a sample that was

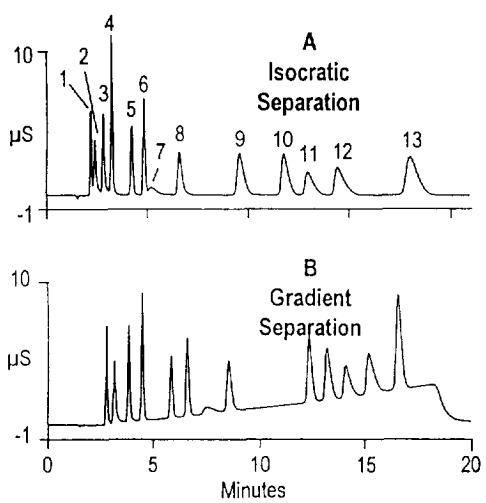

Fig. 9. Comparison of isocratic and gradient separation of anions on an IonPac AS12A column using a borate eluent. Isocratic separation: eluent, 20 mmol/l sodium borate–18 mmol/l sodium hydroxide. Gradient separation: eluent A, water; eluent B, 50 mmol/l sodium borate–37.5 mmol/l sodium hydroxide; gradient, linear from 22% to 73% B in 16 min. Flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 25 µl. Solutes: (1) 5 mg/l fluoride; (2) 10 mg/l acetate; (3) 5 mg/l formate; (4) 5 mg/l chlorite; (5) 5 mg/l bromate; (6) 1 mg/l chloride; (7) 1 mg/l carbonate; (8) 2 mg/l nitrite; (9) 5 mg/l bromide; (10) 5 mg/l chlorate; (11) 5 mg/l nitrate; (12) 10 mg/l orthophosphate; (13) 5 mg/l sulfate.

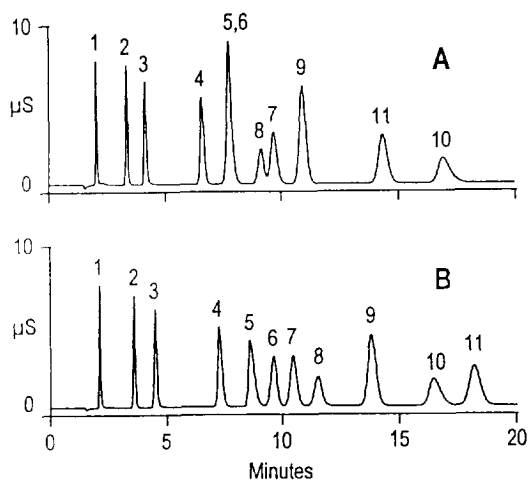

Fig. 10. Separation of common anions, sulfite, selenite, selenate, and arsenate on an IonPac AS12A column. Eluent A, 0.3 mmol/l sodium hydrogencarbonate–2.7 mmol/l sodium carbonate; eluent B, 0.8 mmol/l sodium hydrogencarbonate–2.1 mmol/l sodium carbonate; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 10 µl. Solute concentrations: (1) 3 mg/l fluoride; (2) 5 mg/l chloride; (3) 10 mg/l nitrite; (4) 20 mg/l bromide; (5) 20 mg/l nitrate; (6) 20 mg/l selenite; (7) 30 mg/l orthophosphate; (8) 20 mg/l sulfite; (9) 20 mg/l sulfate; (10) 40 mg/l arsenate; and (11) 20 mg/l selenate.

analysed using a conventional AS4A-SC anion exchanger. The signal appearing shortly after the bromide peak has erroneously been attributed to nitrate. With the baseline-resolved separation between bromide, chlorate and nitrate on IonPac AS12A, the unequivocal identification of this signal is possible. As can be seen from Fig. 7, nitrate is only present in this sample at a low ppb level, while the signal following bromide represents about 10 ppm of chlorate.

By modifying the carbonate-to-hydrogencarbonate ratio in the mobile phase, the analysis speed can be significantly increased. As can be seen from Fig. 8, the rapid elution of anions is accomplished with a mixture of 10.5 mmol/l sodium carbonate and 0.5 mmol/l sodium hydrogencarbonate at a flow-rate of 1.5 ml/min, allowing an analysis time of ca. 5 min. The ionic strength was adjusted so that orthophosphate and sulfate elute before bromide and nitrate. The chromatogram in Fig. 8 clearly demonstrates that under less demanding conditions the AS12A column is capable of the rapid determination of common anions with good resolution.

The chromatograms in Fig. 9 show the use of a borate eluent on the AS12A column for the separation of the common disinfectant by-products. The main advantage of this system is the ability to move the carbonate interference to a location in the chromatogram well away from chlorite and bromate where it does not interfere. Because of the high pH and the different elution properties of the borate eluent, carbonate elutes after chloride, being out of the way of the trace anions found in drinking water. However, as can be seen from the upper chromatogram in Fig. 9, the analysis is lengthy when employing a borate eluent on the AS12A column. Alternatively, a gradient technique can be applied in place of an

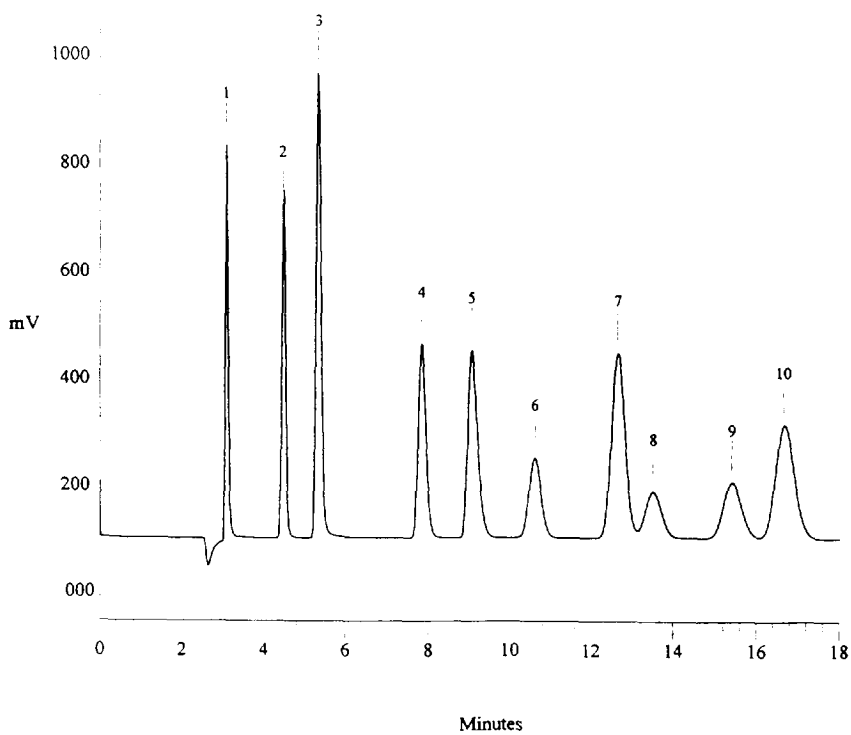

Fig. 11. Separation of common anions and aliphatic dicarboxylic acids on an IonPac AS12A column. Chromatographic conditions as in Fig. 3. Solute concentrations: (1) 3 mg/l fluoride; (2) 4 mg/l chloride; (3) 10 mg/l nitrite; (4) 10 mg/l bromide; (5) 10 mg/l nitrate; (6) 10 mg/l orthophosphate; (7) 10 mg/l sulfate; (8) 10 mg/l malate; (9) 10 mg/l tartrate; and (10) 10 mg/l oxalate.

isocratic eluent system for samples that are not trace in nature. For comparison, the bottom chromatogram in Fig. 9 shows the gradient separation of the same standard. As the baseline shift is modest, borate gradients on the AS12A column are suitable for a number of sample types.

In addition to disinfectant by-product separations, common anions and also sulfite, selenite, selenate and arsenate can be separated on the AS12A column. Under the chromatographic conditions in Fig. 3, resolution problems between nitrate and selenite and between orthophosphate and sulfite are observed (upper chromatogram in Fig. 10). This can be solved by modifying the carbonate-to-hydrogencarbonate ratio. As illustrated in Fig. 10 (bottom chromatogram), a mixture of 2.1 mmol/l sodium carbonate and 0.8 mmol/l sodium hydrogencarbonate results in a baseline-resolved separation of all analytes.

3.2. Organic acid analysis

A common problem with conventional polymer-based anion exchangers such as AS4A-SC and AS9-SC is that the retention behaviour of aliphatic dicarboxylic acids is very similar to that of inorganic anions such as bromide, nitrate, orthophosphate and sulfate. While orthophosphate can be moved out of the way by changing the pH of the mobile phase, the determination of the other three inorganic anions can be interfered with by organic acids, especially in food and beverage samples. Therefore, the retention

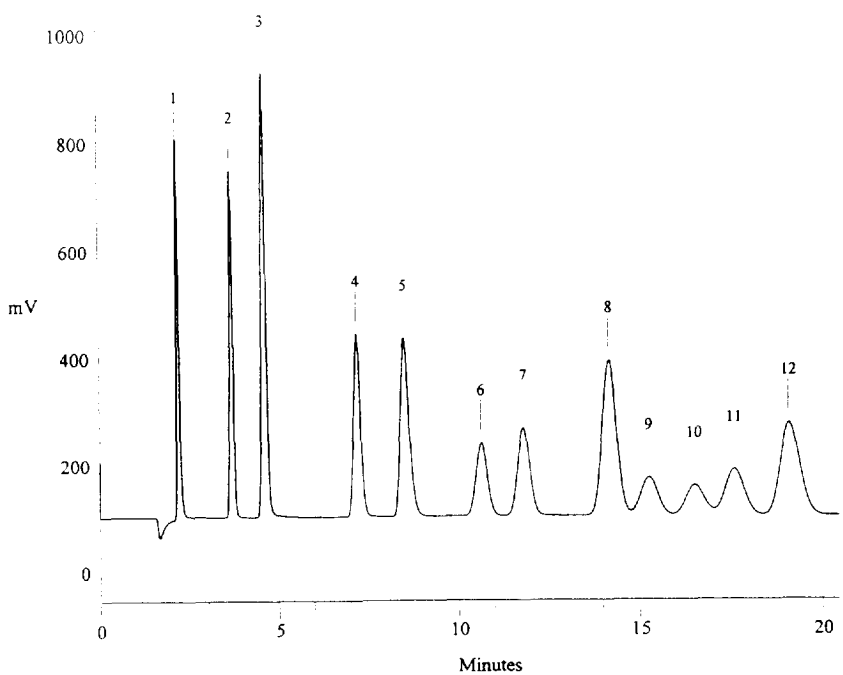

Fig. 12. Separation of common anions, oxy non-metal anions and aliphatic carboxylic acids on an IonPac AS12A column. Chromatographic conditions as in Fig. 10 (bottom chromatogram). Solute concentrations: (1) 3 mg/l fluoride; (2) 4 mg/l chloride; (3) 10 mg/l nitrite; (4) 10 mg/l bromide; (5) 10 mg/l nitrate; (6) 10 mg/l orthophosphate; (7) 10 mg/l sulfite; (8) 10 mg/l sulfate; (9) 10 mg/l malate; (10) 10 mg/l arsenate; (11) 10 mg/l tartrate; (12) 10 mg/l oxalate.

behaviour of malic, tartaric and oxalic acid was investigated under standard chromatographic conditions. The chromatogram in Fig. 11 shows that all three organic acids elute behind sulfate and therefore do not represent an interference in the determination of common inorganic anions.

The modified eluent system described in Fig. 10 (2.1 mmol/l sodium carbonate–0.8 mmol/l sodium hydrogencarbonate) enables all common inorganic anions, and also sulfite, arsenate and the organic acids mentioned above, to be determined in the same isocratic run (Fig. 12).

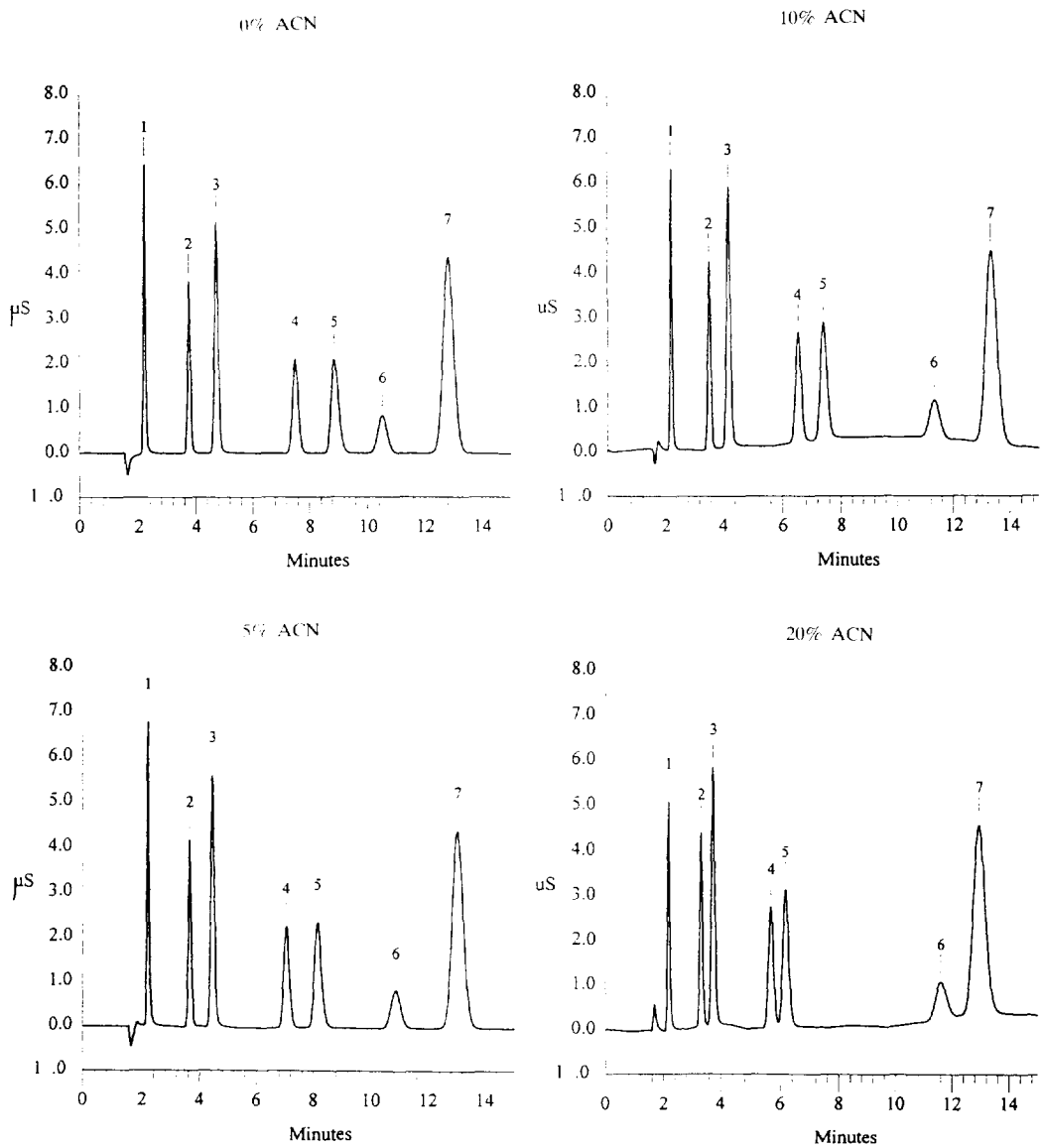

Fig. 13. Influence of organic solvents on the retention of common anions on an IonPac AS12A column. Eluent, 0.3 mmol/l sodium hydrogencarbonate–2.7 mmol/l sodium carbonate–acetonitrile; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection, 25 µl anion standard. Solute concentrations: (1) 3 mg/l fluoride; (2) 4 mg/l chloride; (3) 10 mg/l nitrite; (4) 10 mg/l bromide; (5) 10 mg/l nitrate; (6) 10 mg/l orthophosphate; (7) 20 mg/l sulfate.

3.3. Influence of organic solvents

As the AS12A column is solvent-compatible, organic solvents can be used to remove organic contaminants. In this respect, the resistance to humic acids was investigated. We consider this parameter to be important because most real water samples contain humic acids at various concentration levels. Also, the molecular mass distribution can differ considerably, ranging from 2000 to 500 000. The test was carried out with a humic acid standard with a molecular mass distribution between 600 and 1000. A 300 mg/l aqueous alkaline solution was prepared and injected twenty times. A significant deviation of the retention times of common inorganic anions was not observed. Column degradation was then simulated by injecting a concentrated liquid detergent formula without any sample preparation other than filtration. As expected, a decrease in capacity was observed with every injection. The original separation performance could be restored by rinsing the column with dilute HCl–acetonitrile (20:80, v/v) for 30 min.

Organic solvents can also be used to affect the selectivity of the anion exchanger. The influence of organic solvents on retention was investigated by injecting a standard solution of common inorganic anions under optimized chromatographic conditions (2.7 mmol/l sodium carbonate–0.3 mmol/l sodium hydrogencarbonate), adding different amounts of acetonitrile to the mobile phase. Fig. 13 shows the resulting chromatograms with solvent additions of 5, 10 and 20% (v/v). The effect is remarkable: whereas the retention of fluoride, chloride and sulfate does not change, orthophosphate moves slowly towards the sulfate peak, co-eluting with it at about 40% (v/v) acetonitrile in the mobile phase. As expected, anions undergoing adsorption in addition to the ion-exchange process, such as nitrite (to a certain extent), bromide and nitrate, are less retained with increasing solvent content in the eluent. Thus, polarizable anions strongly retained on an AS12A column can be decreased in retention by adding solvents to the mobile phase. On the other hand, with more than 20% (v/v) acetonitrile in the mobile phase, bromide and nitrate are no longer resolved.

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