New block-grafted anion exchanger for environmental water analysis by ion chromatography

P.E. Jackson*, D.H. Thomas, B. Donovan, C.A. Pohl, R.E. Kiser

Dionex Corporation, 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088-3606, USA

Abstract

The IonPac AS14A is a recently developed stationary phase that was produced using a new block-grafting technique, which enables the preparation of high-water-content anion exchangers with excellent peak shape and good chromatographic efficiency. The performance of this column for the analysis of inorganic anions was compared to that obtained using an IonPac AS4A column, which is specified in US Environmental Protection Agency Method 300.0, in addition to another commonly used alternative; the AS14 column. The AS14A column is available in two different formats; 250×4 mm I.D. (7.0 μm diameter particle) and 150×3 mm I.D. (5.5 μm diameter particle). The IonPac AS14A (in 4 mm I.D. format) was found to provide similar performance to the AS14 column with increased peak efficiency and better pH stability and is a suitable alternative for the analysis of anions in moderate- to high-ionic-strength samples. The IonPac AS14A (in 3 mm I.D. format) provides comparable run times to the AS4A column with better overall peak selectivity and improved fluoride resolution, hence this column would be a suitable column to substitute in place of either the AS4A or AS14 columns for the analysis of inorganic anions in low- to moderate-ionic-strength environmental waters. The AS14A column used with an Atlas electrolytic suppressor provides equivalent method detection limits to those obtained when using a micromembrane suppressor but with the operational convenience of a self-regenerating suppressor. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Anion exchangers; Stationary phases, LC; Inorganic anions

1. Introduction

Ion chromatography (IC) is widely employed for the determination of inorganic anions in environmental waters, such as drinking water, surface water and wastewater. In the the USA, the National Primary Drinking Water Standards specify a maximum contaminant level (MCL) for a number of inorganic anions, including fluoride, nitrite and nitrate. The MCLs are specified to minimize potential health effects arising from ingestion of these anions in drinking water [1]. Other common anions, such as chloride and sulfate, are considered secondary contaminants, and are regulated under the US Secondary Drinking Water Standards, which are guidelines regarding taste, odor, color and aesthetic effects [2]. In addition, the discharge of these inorganic anions is regulated under the Clean Water Act, which has the goal of reducing the discharge of pollutants into USA waters.

IC is an approved method for the analysis of inorganic anions, as specified by a number of regulatory and standards organizations, including the US Environmental Protection Agency (EPA), American Society for Testing and Materials (ASTM), Standard Methods, the German ISO and DIN, the

---

*Corresponding author. Tel.: +1-408-7370-700; fax: +1-408-7309-403.

E-mail address: peter_jackson@dionex.com (P.E. Jackson).

French AFNOR, and the Italian UNICHIM [3]. The majority of these approved methods are based on the original version of EPA Method 300.0, which was first approved for compliance monitoring of inorganic anions in drinking water in the mid-1980s [4]. Method 300.0 specifies the use of an IonPac AS4A anion-exchange column with a carbonate–hydrogen-carbonate eluent and suppressed conductivity detection for the determination of inorganic anions in environmental waters. The method allows for the use of an alternative anion separator column provided that comparable resolution of peaks is obtained and that method quality control (QC) requirements can be met [4].

In this paper, we discuss the use of a new ion-exchange phase for the analysis of inorganic anions in environmental waters. The IonPac AS14A was produced using a recently developed block-grafting technique, which enables the preparation of high-water-content anion exchangers with excellent peak shape and good chromatographic efficiency. The performance of this column for EPA Method 300.0 will be compared to that of the AS4A column, in addition to another widely used alternative, the AS14 column. The method detection limits (MDLs), linear range, and analyte recoveries obtained from environmental waters will be described. A comparison of MDLs obtained using the AS14A column with an anion self regenerating suppressor (ASRS), an anion Atlas electrolytic suppressor (AAES), and an anion micromembrane suppressor (AMMS), will also be presented.

2. Experimental

2.1. Instrumentation

Two IC systems were used for this work, a Dionex (Sunnyvale, CA, USA) DX-120 dedicated ion chromatograph with an AS40 automated sampler; and a DX-600 system consisting of a GS50 gradient pump, an AS50 automated sampler, a CD25 conductivity detector, and an LC20 chromatography enclosure. Dionex PeakNet Chromatography Workstations were used for system control and data collection. Dionex IonPac AS4A-SC, AS14 and AS14A analytical columns and their respective guard

columns, AG4A-SC, AG14 and AG14A, were used for all separations. Chemical suppression was achieved using a Dionex ASRS-ULTRA, operated in recycle mode. An AAES operated in recycle mode and an AMMS operated in displacement chemical regeneration mode were also used for the MDL comparison.

2.2. Reagents and procedures

All solutions were prepared from analytical-reagent grade chemicals in 18 MΩ water, obtained from a Water Pro PS purification system (Labconco, Kansas City, MO, USA). Commercially available (Dionex) 1000 mg/l stock standards of fluoride, chloride, and sulfate were used, while 1000 mg/l stock solutions of nitrite, bromide, nitrate, and phosphate were prepared from their analytical-reagent grade sodium salts (EM Science, Gibbstown, NJ, USA). Stock standards were stored at 4°C and were all stable for at least 1 month. Working standards were prepared fresh daily. Table 1 shows the concentration of MDL standards 1 and 2, and the concentration of the quality control sample (QCS) used to determine the retention time and peak area precision. Commercially available (Dionex) eluent concentrates were used to prepare the eluents for each of the columns.

All water samples were filtered through 0.45-μm syringe filters (Gelman, Ann Arbor, MI, USA) prior to injection, with the exception of the domestic wastewater sample, which was passed through a preconditioned C_{18} Sep-Pak cartridge (Waters, Milford, MA, USA) then filtered before injection. The soil sample was prepared by placing 10 g of dried soil in a 250-ml beaker and adding 18 MΩ water to a total volume of 100 ml. The sample was extracted for 30 min in an ultrasonic bath, allowed to settle and filtered through a 0.45-μm syringe filter before injection.

3. Results and discussion

3.1. IonPac AS4A-SC performance

EPA Method 300.0, which was published in the mid-1980s, specifies the use of an IonPac AS4A

Table 1
Anion concentration of MDL standards 1 and 2 and QCS standard

Anion	MDL calculation standard 1 (mg/l)	MDL calculation standard 2 (mg/l)	QCS standard for RSD calculation (mg/l)
Fluoride	0.025	0.013	2
Chloride	0.010	0.005	20
Nitrite	0.025	0.013	2
Bromide	0.050	0.025	2
Nitrate	0.045	0.023	10
Orthophosphate	0.045	0.023	2
Sulfate	0.050	0.025	60

column for the separation of inorganic anions. The method allows for the use of an alternative column provided that comparable peak resolution is obtained and that method QC requirements can be met [4]. Table 2 shows the characteristics of modern alternatives to the original AS4A; including the current solvent compatible version of this column, the IonPac AS4A-SC; the grafted AS14; and the new block-grafted AS14A, which is available in both 4 mm and 3 mm I.D. formats.

Fig. 1 shows a typical chromatogram of a standard containing low-mg/l levels of inorganic anions obtained using an IonPac AS4A-SC column operated with an ASRS in recycle mode. The AS4A-SC has selectivity similar to that of the AS4A column originally specified in Method 300.0, although the substrate of the AS4A-SC is ethylvinylbenzene (EVB) crosslinked with 55% divinylbenzene (DVB), which makes the column 100% solvent compatible. All the anions are resolved within a total run time of
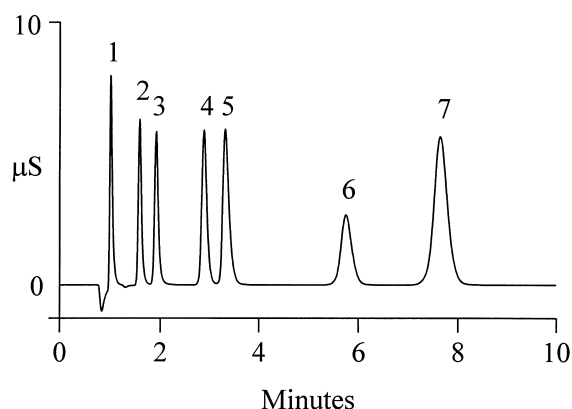

Fig. 1. Separation of inorganic anion standard obtained using an AS4A-SC column. Conditions: column, IonPac AS4A-SC; eluent, 1.8 mM sodium carbonate–1.7 mM sodium hydrogencarbonate; flow-rate, 2.0 ml/min; detection, ASRS-ULTRA operated at 50 mA in recycle mode; injection volume, 50 μl, solutes, 1=fluoride (2 mg/l); 2=chloride (3 mg/l); 3=nitrite (5 mg/l); 4=bromide (10 mg/l); 5=nitrate (10 mg/l); 8=phosphate (15 mg/l); 7=sulfate (15 mg/l).

Table 2
Characteristics of anion-exchange columns investigated

Column type[a]	AS4A-SC	AS14	AS14A (4 mm I.D.)	AS14A (3 mm I.D.)
Particle diameter (μm)	13	9	7	5.5
Particle porosity	Microporous	Macroporous	Macroporous	Macroporous
Resin crosslinking (%)	55	55	55	55
Column capacity (μequiv.column)	20	65	120	30
Hydrophobicity	Medium–low	Medium–high	Medium–high	Medium–high
Functional group	Quaternary amine	Quaternary amine	Quaternary amine	Quaternary amine
Latex diameter	90 nm	Grafted	Block-grafted	Block-grafted
Latex crosslinking	0.5%	Grafted	Block-grafted	Block-grafted
pH stability	0–14	2–11	0–14	0–14
Solvent compatibility (%)	0–100	0–100	0–100	0–100

[a] A 250×4 mm I.D. column.

Table 3
Linearity, MDLs, retention time and peak area precision obtained for inorganic anions using Method 300.0 with an IonPac AS4A-SC column and an ASRS operated in recycle mode

Anion[a]	Range (mg/l)	Linearity (r^2)	Calculated MDL (µg/l)	t_R precision (RSD, %)	Area precision (RSD, %)
Fluoride	0.1–100	0.9971	5.9	0.48	0.67
Chloride	0.2–200	0.9996	2.3	0.30	0.47
Nitrite	0.1–100	0.9997	5.7 (1.8 as NO_2–N)	<0.05	0.53
Bromide	0.1–100	0.9967	9.7	<0.05	0.13
Nitrate	0.1–100	0.9969	6.2 (1.4 as NO_3–N)	0.40	0.17
Orthophosphate	0.1–100	0.9967	17.8 (5.8 as PO_4–P)	0.30	0.35
Sulfate	0.2–200	0.9975	6.7	<0.05	0.14

[a] A 50-µl injection was used with a DX-120 IC system.

8 min. The performance of Method 300.0 using the AS4A-SC column was evaluated by firstly determining method linearity for inorganic anions over a seven-point calibration range. Method detection limits were derived by calculating the standard deviation of seven replicates of a low-level standard (MDL standard 1 shown in Table 1), as described in Method 300.0 [4]. The retention time (t_R) and peak area precision (expressed as RSD, %) were determined from seven replicate injections of a quality control sample (also shown in Table 1).

Table 3 shows the linear concentration ranges investigated, the resulting coefficients of determination (r^2), calculated MDLs for each anion, along with the typical retention time and peak area precision data that can be obtained for the analysis of low-mg/l levels of inorganic anions. In general, the

method provides acceptable linearity, the MDLs are in the low-ppb range, and good t_R and peak area precision are obtained. The performance of methods used for environmental analysis is typically validated through single- and multi-operator precision and bias studies on spiked samples. Table 4 shows typical recovery results obtained when using the IonPac AS4A-SC column for inorganic anions spiked into various environmental water matrices. The samples were spiked with the analytes at approximately the same levels as specified in EPA Method 300.0. Acceptable recovery data (i.e., 80–120%) were obtained for the inorganic anions in most matrices, although the recovery obtained for fluoride in domestic wastewater was poor because of interference from organic acids. Also, the recoveries for nitrite and nitrate were not as expected in the domestic waste-

Table 4
Single operator recovery results obtained for inorganic anions spiked in environmental water matrices using the IonPac AS4A-SC column

Anion	Drinking water Amount added (mg/l)	Recovery (%)	Raw water Amount added (mg/l)	Recovery (%)	Surface water Amount added (mg/l)	Recovery (%)	Domestic wastewater Amount added (mg/l)	Recovery (%)	Industrial wastewater Amount added (mg/l)	Recovery (%)	Soil extract Amount added (mg/l)	Recovery (%)
Fluoride	1	93.9	1	96.5	1	109.0	1	57.0	1	88.0	2	99.0
Chloride	10	97.4	20	83.2	40	81.4	20	82.7	20	100.8	5	100.2
Nitrite	2	91.6	2	102.1	4	105.0	2	217.0[a]	2	98.0	2	102.5
Bromide	2	98.7	2	96.7	2	101.0	2	86.5	2	92.0	2	91.0
Nitrate	5	92.4	5	94.4	10	96.7	5	6.8[a]	5	96.2	5	90.2
Orthophosphate	10	95.0	10	95.4	10	107.9	20	101.6	20	98.8	20	111.7
Sulfate	20	97.5	40	106.8	40	106.4	40	90.6	40	105.9	20	96.6

[a] Sample stored for longer than recommended holding time; inappropriate recovery due to microbial action.

water sample. However, at the time of these analyses, the sample had been stored (at 4°C) for longer that the recommended holding time for nitrite/nitrate of 2 days [4]. In this case, the unexpected recoveries may be attributed to the presence of nitrifying/denitrifying microbes in the sample rather than any chromatographic resolution problems.

Hence, the modest capacity IonPac AS4A column specified in Method 300.0, along with the AS4A-SC column, is most appropriate for the analysis of anions in low ionic strength, well characterized samples, such as drinking and surface waters, as shown in Fig. 2. This column is not recommended for the analysis of fluoride in complex samples which contain small organic acids, such as domestic wastewater. There remains considerable interest in the development of a column with similar characteristics to the AS4A-SC column, i.e., rugged with good peak efficiency, but with improved selectivity to allow resolution of fluoride from the column void volume and also from organic acids, such as acetate and formate.

3.2. IonPac AS14 performance

Over the past decade or so, significant effort has been put into the development of improved ion-exchange phases for the routine determination of inorganic anions. Fig. 3 shows a chromatogram obtained using the most widely employed alternative

to the AS4A for the analysis of inorganic anions; the IonPac AS14 column. This column is packed with a methacrylate-based functional group grafted onto the surface of a macroporous resin consisting of EVB crosslinked with 55% DVB. The AS14 provides improved overall peak resolution compared to the AS4A column, including complete separation of fluoride from the column void peak, as shown in Fig. 3. The improved selectivity and higher capacity of the AS14 column (65 μequiv./column compared to 20 μequiv./column for the AS4A) also allows improved resolution of chloride and nitrite, which is important in environmental water analysis. One drawback of using the grafted, higher capacity AS14 column is that lower peak efficiencies are obtained compared to using the latex-agglomerated AS4A-SC column.

Table 5 shows performance data obtained for Method 300.0 using the AS14 column operated with an ASRS in recycle mode. The data is similar to that obtained using the AS4A-SC column (shown in Table 3), although the MDLs were slightly higher due to the lower efficiency and higher capacity of the AS14 column. However, the benefits of improved selectivity are seen in Table 6, which shows typical recovery results obtained using the AS14 column for inorganic anions spiked into environmental water samples. In this case, acceptable recovery data (i.e., 80–120%) were obtained for the inorganic anions in all matrices when using the AS14 column, with the
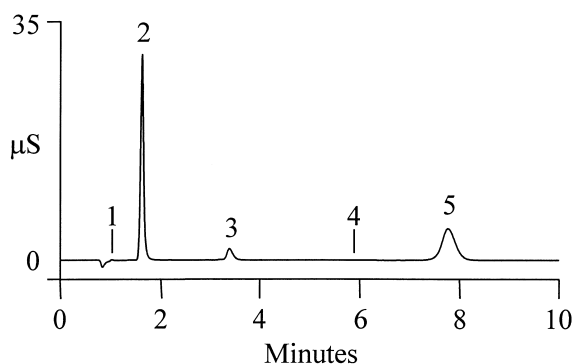

Fig. 2. Analysis of inorganic anions in drinking water. Conditions: as for Fig. 1, except; sample, Sunnyvale, CA, USA, tapwater; solutes, 1=fluoride (0.03 mg/l); 2=chloride (9.3 mg/l); 3=nitrate (2.5 mg/l); 4=phosphate (0.10 mg/l); 5=sulfate (10.9 mg/l).
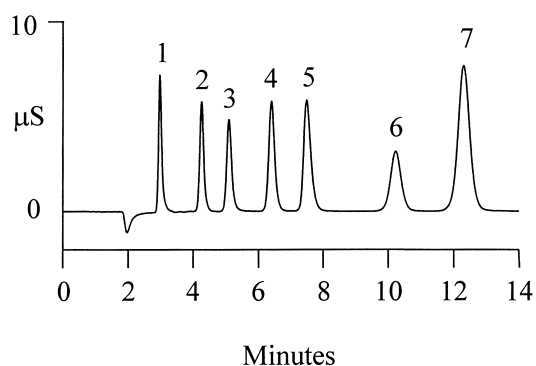

Fig. 3. Separation of inorganic anion standard obtained using an AS14 column. Conditions: as in Fig. 1, except; column, IonPac AS14; eluent, 3.5 m*M* sodium carbonate–1.0 m*M* sodium hydrogencarbonate; flow-rate, 1.2 ml/min; detection, ASRS-ULTRA operated at 100 mA in recycle mode.

Table 5
Linearity, MDLs, retention time and peak area precision obtained for inorganic anions using Method 300.0 with an IonPac AS14 column and an ASRS operated in recycle mode

Anion[a]	Range (mg/l)	Linearity (r^2)	Calculated MDL (μg/l)	t_R precision (RSD, %)	Area precision (RSD, %)
Fluoride	0.1–100	0.9971	5.9	0.48	0.67
Chloride	0.2–200	0.9996	2.3	0.30	0.47
Nitrite	0.1–100	0.9997	5.7	<0.05	0.53
			(1.8 as NO_2–N)		
Bromide	0.1–100	0.9967	9.7	<0.05	0.13
Nitrate	0.1–100	0.9969	6.2	0.40	0.17
			(1.4 as NO_3–N)		
Orthophosphate	0.1–100	0.9967	17.8	0.30	0.35
			(5.8 as PO_4–P)		
Sulfate	0.2–200	0.9975	6.7	<0.05	0.14

[a] A 50-μl injection was used with a DX-120 IC system.

exception of nitrite and nitrate in the same domestic wastewater sample. However, as discussed previously, this was again due to the presence of nitrifying/denitrifying microbes rather than any chromatographic resolution problems. Fig. 4 shows a chromatogram of inorganic anions in a domestic wastewater sample obtained using the AS14 column. This chromatogram clearly shows that fluoride is well resolved from the column void volume and also from the later eluting (acetate) peak. Hence, the selectivity and capacity of the AS14 column make it suitable for the routine determination of anions in moderate-ionic-strength environmental waters.

3.3. IonPac AS14A performance

While the AS14 column provides suitable per-

formance for the determination of anions in most environmental water samples, the peak efficiency is lower and the total run time is longer than that obtained using the AS4A column. Also, very high-ionic-strength samples are best analyzed using a still higher capacity column, such as the IonPac AS9-HC column [5]. The AS14A stationary phase material was developed to provide superior performance for inorganic anion analysis in the widest range of environmental waters. The AS14A column is available in two different formats; 150×3 mm I.D. (5.5 μm diameter particle) and 250×4 mm I.D. (7.0 μm diameter particle). The 4 mm I.D. format provides improved performance to the existing AS14 grafted column. Fig. 5 shows a comparison of the chromatograms of a low-ppm level anion standard (including acetate) obtained using the IonPac AS14 (a) and the

Table 6
Single operator recovery results obtained for inorganic anions spiked in environmental water matrices using the IonPac AS14 column

Anion	Drinking water		Raw water		Surface water		Domestic wastewater		Industrial wastewater		Soil extract	
	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)
Fluoride	1	91.5	1	85.1	1	101.0	1	90.8	1	90.1	2	101.1
Chloride	10	94.6	20	84.0	40	83.6	20	87.3	20	96.7	5	96.7
Nitrite	2	103.1	2	92.0	4	100.2	2	0.0[a]	2	98.2	2	89.3
Bromide	2	96.1	2	95.6	2	93.3	2	96.8	2	96.2	2	89.9
Nitrate	5	87.2	5	89.4	10	93.2	5	15.3[a]	5	95.1	5	92.8
Orthophosphate	10	93.8	10	94.2	10	106.4	20	94.3	20	95.9	20	111.0
Sulfate	20	96.1	40	106.6	40	106.1	40	91.5	40	102.0	20	94.7

[a] Sample stored for longer than recommended holding time; inappropriate recovery due to microbial action.
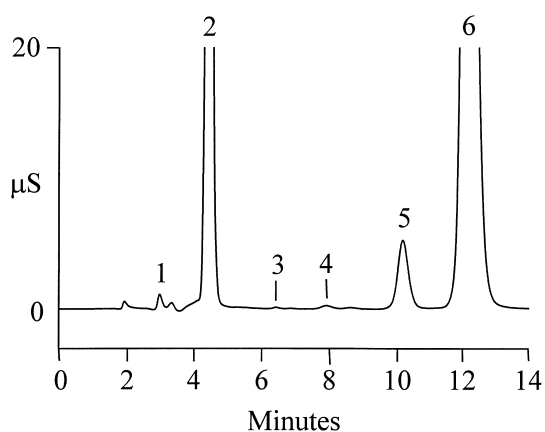
Fig. 4. Analysis of inorganic anions in domestic wastewater. Conditions: as in Fig. 3, except; sample, wastewater from a septic tank; solutes, 1=fluoride (0.34 mg/l); 2=chloride (70.4 mg/l); 3=bromide (0.13 mg/l); 4=nitrate (0.31 mg/l); 5=phosphate (24.0 mg/l); 6=sulfate (154 mg/l).

IonPac AS14A (b) columns. Similar selectivity is obtained with both columns, although the higher capacity AS14A (120 μequiv./column) requires the use of a higher ionic strength eluent in order to achieve a similar total run time. The block-grafting technique used to produce the AS14A column produces a more uniform functionalized layer on the column surface, resulting in improved peak efficiencies, as can be seen for peaks 5–8 in Fig. 5b.

Fig. 6 shows a comparison of the chromatograms of a low-ppm level anion standard (including acetate) obtained using the IonPac AS4A (a) and the 150×3.0 mm I.D. AS14A column (b). The eluent flow-rate and injection volume for the 3 mm I.D. column are adjusted by a factor of 0.5×, which is approximately in proportion to the ratio of the square of the I.D.s of the two columns. The 3 mm I.D. AS14A column provides similar run times and peak responses compared to the AS4A-SC column, although the AS14A provides significantly improved separation of fluo-
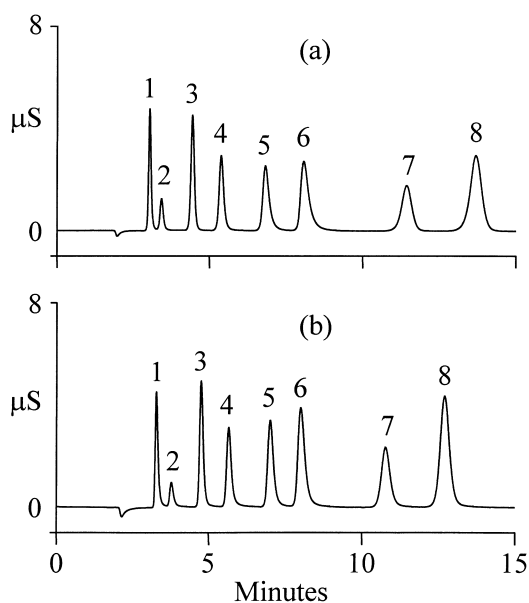

Fig. 5. Comparison of the AS14 (a) and AS14A (b) columns for the separation of inorganic anions and acetate. Conditions: as in Fig. 3, except (b); column, IonPac AS14A (4 mm I.D.); eluent, 8.0 mM sodium carbonate–1.0 mM sodium hydrogencarbonate; flow-rate, 1.0 ml/min; solutes (a+b), 1=fluoride (1 mg/l); 2=acetate (4 mg/l); 3=chloride (2 mg/l); 4=nitrite (3 mg/l), 5=bromide (5 mg/l); 6=nitrate (5 mg/l); 7=phosphate (8 mg/l); 8=sulfate (6 mg/l).
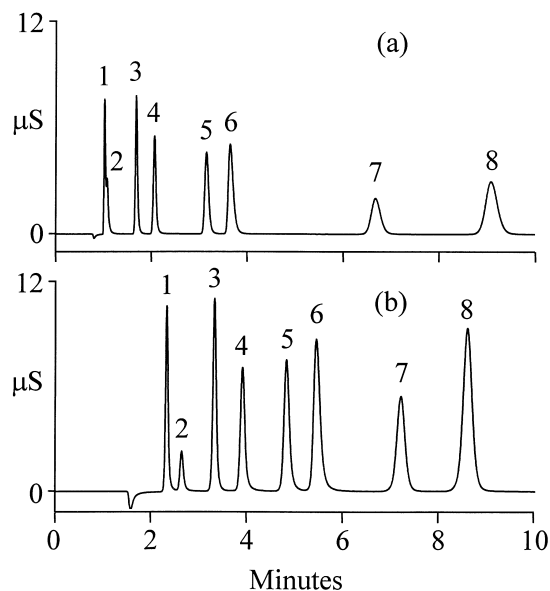

Fig. 6. Comparison of the AS4A (a) and AS14A (b) columns for the separation of inorganic anions and acetate. Conditions: as in Fig. 1, except (b); column, IonPac AS14A (3 mm I.D.); eluent, 8.0 mM sodium carbonate–1.0 mM sodium hydrogencarbonate; flow-rate, 0.5 ml/min; detection, ASRS-ULTRA (2 mm) operated at 50 mA in recycle mode; injection volume, 25 μl; solutes (a+b), 1=fluoride (1 mg/l); 2=acetate (4 mg/l); 3=chloride (2 mg/l); 4=nitrite (3 mg/l); 5=bromide (5 mg/l); 6=nitrate (5 mg/l); 7=phosphate (8 mg/l); 8=sulfate (6 mg/l).

Table 7
Linearity, MDLs, retention time and peak area precision obtained for inorganic anions using Method 300.0 with an IonPac AS14A column (4 mm I.D.) and an ASRS operated in recycle mode

Anion	Range (mg/l)	Linearity (r^2)	Calculated MDL[a] (μg/l)	Calculated MDL[b] (μg/l)	t_R precision (RSD, %)	Area precision (RSD, %)
Fluoride	0.1–100	0.9983	5.7	3.1	0.16	0.35
Chloride	0.2–200	0.9996	5.9	5.4	0.12	0.14
Nitrite	0.1–100	0.9999	7.1	5.7	0.12	0.39
			(2.2 as NO_2–N)	(1.8 as NO_2–N)		
Bromide	0.1–100	0.9979	10.1	8.9	0.15	0.44
Nitrate	0.1–100	0.9979	9.3	7.7	0.15	0.37
			(2.1 as NO_3–N)	(1.7 as NO_3–N)		
Orthophosphate	0.1–100	0.9981	28.1	15.6	0.10	0.42
			(9.2 as PO_4–P)	(5.1 as PO_4–P)		
Sulfate	0.2–200	0.9988	12.0	9.6	0.10	0.21

[a] A 250×4.0 mm I.D. column and 50-μl injection were used with a DX-600 IC system.
[b] A 150×3.0 mm I.D. column and 25-μl injection were used with a DX-600 IC system.

ride from the column void volume, complete resolution of fluoride and acetate, and better overall peak selectivity. Table 7 summarizes Method 300.0 performance with the AS14A column. The MDLs obtained with the 4 mm I.D. column are slightly higher than for the existing AS14 (due to higher capacity), while the 3 mm I.D. column gives similar MDLs compared to the AS4A-SC column. Table 8 shows recoveries for anions spiked into various environmental water matrices using the AS14A (4 mm I.D.) column. In this instance, quantitative recoveries were obtained (i.e., 80–120%) for all analytes in all matrices when using the AS14A column. Similar results were obtained when using the 3 mm I.D. column.

3.4. Comparison of suppressor performance

All the data shown above were generated using Anion ASRS-ULTRA suppressors operated in the recycle mode. Since the electrolysis of water is utilized as the regenerant ion source, no other chemical feed is required, simplifying the operation of the IC system. However, this approach generates higher baseline noise than a conventional membrane-based (AMMS) device operated in chemical regeneration mode. The AAES is a new suppressor device with the operational convenience of an electrolytically regenerated ASRS and the signal-to-noise performance of an AMMS. This fifth-generation suppressor device is based upon the principles of "ion

Table 8
Single operator recovery results obtained for inorganic anions spiked in environmental water matrices using the IonPac AS14A (4 mm I.D.) column

Anion	Drinking water		Raw water		Surface water		Domestic wastewater		Industrial wastewater		Soil extract	
	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)
Fluoride	1	106.9	1	93.0	1	106.0	1	103.0	1	99.2	2	101.3
Chloride	10	92.0	20	113.7	40	111.4	20	108.3	20	104.1	5	83.8
Nitrite	2	89.1	2	100.8	4	102.9	2	96.0	2	93.2	2	91.1
Bromide	2	98.9	2	85.3	2	99.4	2	85.5	2	86.6	2	88.0
Nitrate	5	103.1	5	97.2	10	93.3	5	85.0	5	85.7	5	107.2
Orthophosphate	10	102.7	10	93.5	10	95.5	20	101.9	20	97.0	20	111.5
Sulfate	20	89.6	40	90.3	40	90.2	40	80.6	40	107.2	20	104.8

Table 9
Method detection limits obtained for inorganic anions using an IonPac AS14A column (3 mm I.D.) with ASRS, AAES and AMMS suppressors

Anion	Calculated MDL[a] (µg/l)	Calculated MDL[b] (µg/l)	Calculated MDL[c] (µg/l)	Calculated MDL[d] (µg/l)	Calculated MDL[e] (µg/l)
Fluoride	3.1	0.7	1.1	1.4	1.3
Chloride	5.4	2.5	1.8	1.1	0.7
Nitrite	5.7	2.2	3.1	3.3	2.8
	(1.8 as NO_2–N)	(0.7 as NO_2–N)	(1.0 as NO_2–N)	(1.0 as NO_2–N)	(0.9 as NO_2–N)
Bromide	8.9	4.8	2.2	3.8	5.6
Nitrate	7.7	3.6	2.6	4.8	4.9
	(1.7 as NO_3–N)	(0.8 as NO_3–N)	(0.6 as NO_3–N)	(1.1 as NO_3–N)	(1.1 as NO_3–N)
Orthophosphate	15.6	10.8	10.2	7.3	4.8
	(5.1 as PO_4–P)	(3.5 as PO_4–P)	(3.3 as PO_4–P)	(2.4 as PO_4–P)	(1.6 as PO_4–P)
Sulfate	9.6	7.8	5.7	4.8	8.6

[a] ASRS, in recycle mode, MDL 1.
[b] AAES, 30 mA in recycle mode, MDL 1.
[c] AMMS-III, in DCR mode, MDL 1.
[d] AAES, 30 mA in recycle mode, MDL 2.
[e] AMMS-III, in DCR mode, MDL 2.

reflux'', an ion-exchange technique in which passing water through an electrically polarized resin bed electrolytically generates the source of the eluent as well as its means of suppression [6]. The AAES provides the benefits of continuous regeneration, the ability to withstand high back pressures, the low noise performance of the AMMS devices, but with the convenience of an ASRS in recycle mode.

Table 9 shows a comparison of the MDLs obtained using the IonPac AS14A (3 mm I.D.) with an ASRS operated in recycle mode, an AAES operated in recycle mode, and an AMMS-III operated in displacement chemical regeneration (DCR) mode. The AAES and AMMS devices produce similar MDLs, which are on the order of 2–3-times lower than those obtained with the ASRS operated in recycle mode. The injection of seven replicates of the lower concentration MDL standard 2 with AAES and AMMS devices did not significantly affect the calculated MDLs, indicating that the results obtained using MDL standard 1 were valid.

4. Conclusions

The new IonPac AS14A (in 4 mm I.D. format) provides similar performance to the existing AS14 column with increased peak efficiency and better pH stability. The relatively high capacity of the AS14A packing material makes this column a suitable alternative to both the AS14 and AS9-HC columns when analyzing anions in moderate- to high-ionic-strength samples. The IonPac AS14A (in 3 mm I.D. format) provides comparable run time to the AS4A column with better overall peak selectivity, improved separation of fluoride from the column void volume and complete resolution of fluoride and acetate. This column would be a suitable column to substitute in place of either the AS4A or AS14 columns for the analysis of inorganic anions in low- to moderate-ionic-strength environmental waters.

The AAES, a fifth-generation suppressor device, provides similar MDLs to a conventional membrane-based suppressor, which are on the order of 2–3-times lower than those obtained with an electrolytic self-regenerating suppressor. Hence, the continuously regenerated AAES device provides the operational convenience of an ASRS device and equivalent signal-to-noise and MDL performance of an AMMS device.

References

[1] EPA, Fed. Reg. 63 (160) (1998) FR 44511.

[2] EPA, Fed. Reg. 59 (145) (1994) FR 38709.

[3] P.E. Jackson, C. Weigert, C.A. Pohl, C. Saini, J. Chromatogr. A 884 (2000) 175.

[4] Method 300.0, US Environmental Protection Agency, Cincinnati, OH, 1993.

[5] L.K. Jackson, R.J. Joyce, M. Laikhtman, P.E. Jackson, J. Chromatogr. A 829 (1998) 187.

[6] H. Small, J. Riviello, Anal. Chem. 70 (1998) 2205.