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Determination of inorganic anions in environmental waters with a hydroxide-selective column

P.E. Jackson*, C. Weigert, C.A. Pohl, C. Saini

Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3606, USA

Abstract

US Environmental Protection Agency Method 300.0 specifies the use of an IonPac AS4A anion-exchange column with a carbonate–hydrogencarbonate eluent and suppressed conductivity detection for the determination of inorganic anions in environmental waters by ion chromatography. Hydroxide eluents have not typically been used for the routine analysis of common inorganic anions due to the lack of an appropriate hydroxide selective column and the difficulty in preparing contaminant free hydroxide eluents. The use of ion chromatography with a hydroxide-selective IonPac AS17 column, automated eluent generation and potassium hydroxide gradient represents a new approach to the routine determination of inorganic anions in environmental waters. This new approach, which is a modification of Method 300.0, allows equivalent method performance with improved linearity, precision, and method detection limits. The AS17 column provides superior retention of fluoride from the column void volume and improved resolution from small organic acids, such as formate and acetate, compared to the AS4A column. Quantitative recoveries were obtained for all the common inorganic anions spiked into typical environmental waters using this new approach, and the Performance Based Measurement System Tier 1 method validation quality control acceptance criteria are well within the acceptable ranges defined by Method 300.0. In addition, the EG40 eluent generator eliminates the need to manually prepare eluents, increasing the level of automation and ease-of-use of the ion chromatography system. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of inorganic anions in environmental waters, such as drinking water, surface water, and wastewater, is perhaps the most widely used application of ion chromatography (IC) worldwide. The US National Primary Drinking Water Standards specifies 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 inges-

tion 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 certain 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 waters in the USA.

IC has been approved for compliance monitoring of these inorganic anions in drinking water since the mid-1980s, as described in US Environmental Protection Agency (EPA) Method 300.0 [3]. This same method received interim approval for the

*Corresponding author.

analysis of inorganic anions in wastewater under the National Pollution Discharge Elimination System (NPDES) permits program in 1992. Many industrial countries have similar health and environmental standards to the USA, and a considerable number of regulatory IC methods, most of which are similar to EPA Method 300.0, have been published worldwide for the determination of inorganic anions in environmental waters. For instance, Germany Methods DIN 38 405 (D 20) and DIN ISO 10 304-1 are similar to EPA Method 300.0 [4]. French Method AFNOR T90-042 is again similar to EPA Method 300.0, as is the Italian method UNICHIM 926 (1991). Several IC methods are approved in Japan for the analysis of anions in matrices such as industrial waters (K0101), industrial wastewater (K0102), mine water, and wastewater (M0202) [4].

EPA Method 300.0 specifies the use of an IonPac AS4A anion-exchange column with a carbonate–hydrogencarbonate eluent and suppressed conductivity detection for the determination of inorganic anions in environmental waters, such as drinking water, wastewater, and aqueous solid extracts. Hydroxide eluents have not typically been used for the routine analysis of common inorganic anions due to the lack of an appropriate hydroxide selective column and the difficulty in preparing contaminant free hydroxide eluents. In this paper, we describe the use of automated eluent generation combined with a new hydroxide selective, anion-exchange column, the IonPac AS17, for the determination of inorganic anions in environmental matrices. The linear range, method detection limits, potential interferences, and application of this approach to a variety of environmental waters will be described.

As the use of a hydroxide eluent and optional column is considered a modification of Method 300.0, the EPA Performance Based Measurement System (PBMS) method validation process will also be discussed. The Tier 1 method validation requirements for an individual laboratory will be outlined and an example of the initial precision and recovery data obtained using the IonPac AS17 column with a hydroxide gradient will be presented, along with comparisons between using this new approach and the one described in Method 300.0 for the analysis of inorganic anions in environmental waters.

2. Experimental

2.1. Instrumentation

The ion chromatograph used for this work was a Dionex (Sunnyvale, CA, USA) DX-500 System consisting of a GP50 gradient pump, an AS50 automated sampler, a CD20 conductivity detector, and a LC20 Chromatography Enclosure. Dionex IonPac AS4A-SC and AS17 (250×4 mm I.D.) analytical columns and their respective guard columns, AG4A-SC and AG17 (50×4.0 mm I.D.), were used for all separations. An EG40 eluent generator with an EluGen OH cartridge was used in conjunction with the AS17 column. Chemical suppression was achieved using a Dionex ASRS-ULTRA, operated at either 50 or 100 mA in recycle mode. A Dionex PeakNet Chromatography Workstation was used for system control and data collection.

2.2. Reagents and procedures

All solutions were prepared from analytical reagent-grade chemicals in 18 M Ω water, obtained from a Water Pro PS purification system (Labconco, Kansas City, MO, USA). Commercially available (Dionex) 1000 μ g/ml stock standards of fluoride, chloride, and sulfate were used, while 1000 μ g/ml 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. The concentration of the standard used to calculate the method detection limits (MDLs) is shown in Table 1. The concentration of the quality control sample (QCS) used to determine the retention time and peak area precision is also shown in Table 1. A commercially available (Dionex) concentrate was used to prepare the eluent for the AS4A-SC column.

All water samples were filtered through 0.45- μ m syringe filters (Gelman, Ann Arbor, MI, USA) prior to injection, with the exception of the domestic wastewater sample, which was passed through a preconditioned C₁₈ Sep-Pak cartridge (Waters, Milford, MA, USA) then filtered before injection. The

Table 1
Anion concentration of MDL and QCS standards

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

soil sample was prepared by placing 10 g of dried soil in a 250 ml beaker and adding 18 M Ω 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- μ m syringe filter before injection.

3. Results and discussion

3.1. Column characteristics

EPA Method 300.0(A) specifies the use of an IonPac AS4A anion-exchange column with an eluent of 1.8 mM sodium carbonate–1.7 mM sodium hydrogencarbonate for the separation of common inorganic anions [3]. The most recent version of this column, the IonPac AS4A-SC, has the same capacity (20 μ equiv.) and similar selectivity to the AS4A column, although the substrate of the AS4A-SC is ethylvinylbenzene (EVB) cross-linked with 55% divinylbenzene (DVB), which makes the column 100% solvent compatible. The AS4A-SC is a latex agglomerated column, consisting of 160 nm alkanol quaternary ammonium functionalized latex electrostatically bound to 13 μ m sulfonated EVB–DVB core particles. Fig. 1a shows a typical chromatogram of a standard containing low-ppm levels of inorganic anions obtained using an IonPac AS4A-SC column, a carbonate–hydrogencarbonate eluent, and suppressed conductivity detection.

The IonPac AS17 column is also a latex agglomerated column and uses the same sulfonated EVB–DVB substrate material, although with a particle diameter of 10.5 μ m. The outer layer consists of 75

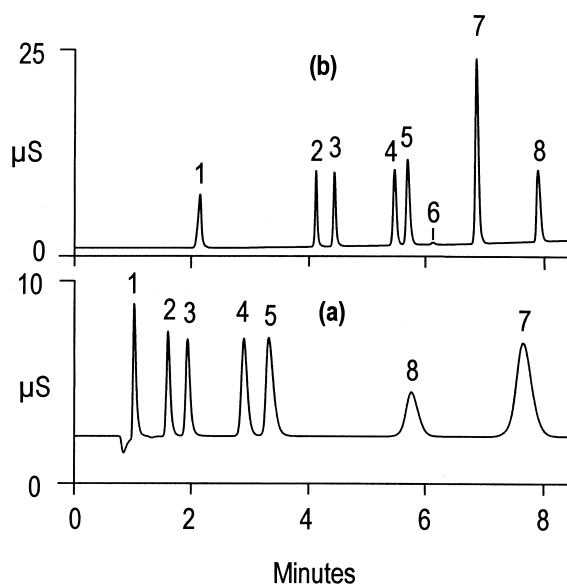


Fig. 1. Separation of inorganic anion standard. Conditions: (a) column, IonPac AS4A-SC; eluent, 1.8 mM sodium carbonate–1.7 mM sodium hydrogencarbonate; flow-rate, 2.0 ml/min; detection, ASRS-ULTRA operated at 50 mA in recycle mode; injection volume, 50 μ l; (b) column, IonPac AS17; eluent, potassium hydroxide generated with an EG40 – 1 mM from 0 to 1.5 min, 1 to 20 mM from 1.5 to 5 min, 20 to 40 mM from 5 to 7 min, 40 mM from 7 to 8.5 min, 1.0 mM from 8.5 to 10 min; flow-rate, 2.0 ml/min; detection, ASRS-ULTRA operated at 100 mA in recycle mode; injection volume, 25 μ l; 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), 6-carbonate, 7-sulfate (15 mg/l), 8-phosphate (15 mg/l).

nm latex functionalized with alkanol quaternary ammonium groups. In the case of the AS17 column, the average number of hydroxyl groups incorporated into the alkanol functionality was higher than with the AS4A-SC column. The net result is a column with similar capacity (30 μ equiv.), higher efficiency, and greater selectivity toward hydroxide eluents (i.e., more hydrophilic) than the AS4A-SC column. Fig. 1b shows a chromatogram of the same inorganic anion standard obtained using an IonPac AS17 column, an hydroxide gradient, and suppressed conductivity detection.

Comparison of the two chromatograms shows that the columns have similar selectivities for the peak pairs of chloride–nitrite and bromide–nitrate, but selectivity differences are evident for the other

peaks. Fluoride is resolved from the column void volume by over 1 min in the chromatogram shown in Fig. 1b, while it is not completely resolved in Fig. 1a. Phosphate elutes after sulfate when using the hydroxide eluent conditions in Fig. 1b, as the higher eluent pH results in increased charge on the polyprotic acid species, hence increased retention. A carbonate peak elutes near nitrate when using the hydroxide eluent with the AS17 column, although this peak is not evident in the chromatogram obtained with the AS4A-SC column. In fact, carbonate essentially co-elutes (as hydrogencarbonate) with chloride under these conditions, although the peak response for carbonate is significantly reduced due to the use of the carbonate–hydrogencarbonate eluent. This can lead to quantitation problems for chloride at high levels of sample carbonate when using the AS4A-SC column.

In addition to fluoride being well resolved from the column void volume, fluoride is also resolved from short chained organic acids on the hydroxide selective column. Fig. 2 shows a chromatogram of an expanded anion standard obtained using the IonPac AS17 column, an hydroxide gradient, and suppressed

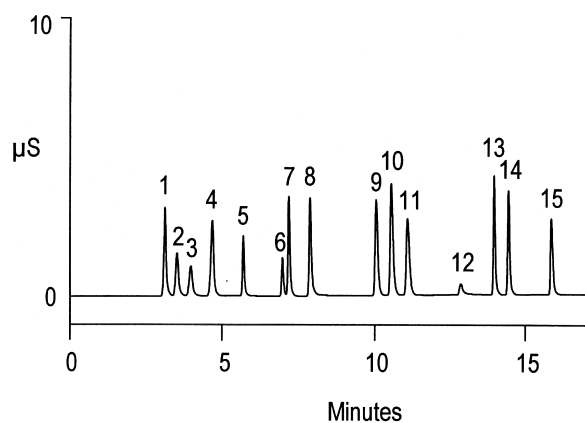


Fig. 2. Separation of expanded anion standard. Conditions: as for Fig. 1b except; eluent, potassium hydroxide generated with an EG40 – 1 mM from 0 to 3 min, 1 to 12 mM from 3 to 10 min, 12 mM to 35 mM from 10 to 14 min, 35 mM from 14 to 17.5 min, 1.0 mM from 17.5 to 20 min; flow-rate, 1.5 ml/min; solutes, 1-fluoride (2 mg/l), 2-acetate (5 mg/l), 3-propionate (5 mg/l), 4-formate (5 mg/l), 5-chlorite (5 mg/l), 6-bromate (5 mg/l), 7-chloride (3 mg/l), 8-nitrite (5 mg/l), 9-bromide (10 mg/l), 10-nitrate (10 mg/l), 11-chlorate (10 mg/l), 12-carbonate, 13-sulfate (15 mg/l), 14-oxalate (5 mg/l), 15-phosphate (15 mg/l).

conductivity detection. Fluoride, acetate, propionate, and formate are completely resolved under these gradient conditions, although the organic acids, while resolved from fluoride, are not completely separated from each other when using the steeper gradient conditions described for Fig. 1. Also, other potential interferences, such as oxyhalide anions (chlorite, bromate, and chlorate) and oxalate are resolved from the common inorganic anions under these conditions. In addition to the selectivity differences, a further benefit to using the AS17 column is that the combination of smaller particle size and the use of gradient elution provides greater peak efficiency, particularly for the later eluting solutes, as evident in Fig. 2.

3.2. Automated eluent generation

Common inorganic anions have not typically been analyzed using hydroxide eluents due to the lack of a suitable hydroxide selective column and also the difficulty in preparing hydroxide eluents. Great care must be taken to minimize contamination of hydroxide by carbonate, which causes a significant baseline shift during the hydroxide gradient. This shift occurs as a result of the relatively high pK_a value of the suppression product (carbonic acid) contributing to increased eluent conductance during the course of the gradient [5]. Also, the presence of carbonate contamination can cause variation in the analyte retention times, particularly for early eluting anions. Consequently, eluents are best prepared from fresh 50% (w/w) sodium hydroxide aqueous solution, rather than pellets. The hydroxide should be weighed and quickly transferred into an eluent bottle containing an appropriate volume of degassed water, which should then be pressurized with helium at 8 p.s.i. (1 p.s.i.=6894.76 Pa) [6]. While the use of an in-line, anion-exchange trap column can reduce the extent of eluent carbonate contamination, a moderate baseline rise is still observed during the hydroxide gradient when using a trap column [6].

Recently, an electrolytic eluent generation device has been produced which automates the production of high purity hydroxide eluents [5]. An eluent of potassium hydroxide is produced in the EG40 eluent generator by pumping deionized water through a KOH generation chamber and applying a d.c. current between the anode and cathode of an OH EluGen

cartridge. Under the applied field, electrolysis of water occurs and hydronium ions generated at the anode in the cartridge displace electrolyte potassium ions across an ion-exchange connector. The potassium ions combine with hydroxide ions generated at the cathode to produce a KOH solution, with the concentration being directly proportional to applied current. The cartridge lifetime would typically be around 2000 h under the conditions shown in Fig. 2 [5]. In addition to eliminating the need to manually prepare eluents, the EG40 offers the added benefit of producing carbonate-free hydroxide eluents on-line. As there is essentially no carbonate contamination, minimal baseline shift is seen during the gradient separation when using this automated eluent generator, as evident in Fig. 2.

3.3. Method performance

The Quality Control section of EPA Method 300.0 requires a demonstration of the linear calibration range, method detection limits, and acceptable instrument performance through the preparation and analysis of a quality control sample (QCS) prior to performing analyses using the method. The performance of Method 300.0 with the AS4A-SC column was evaluated by determining method linearity for inorganic anions over a seven point calibration range. MDLs were calculated by injecting seven replicates of an MDL standard (shown in Table 1), which consisted of reagent water fortified at a concentration of 3–5 times the estimated instrument detection limit [3]. Table 2 shows the linear concentration ranges investigated, the resulting co-

efficients of determination (r^2) and typical calculated MDLs for each anion. The retention time and peak area precision (expressed as RSD) were determined from seven replicate injections of a quality control sample (shown in Table 1), which consisted of method analytes spiked into reagent water. The typical retention time and peak area precision data that can be obtained for the analysis of low-mg/l levels of inorganic anions by IC using the IonPac AS4A-SC column are shown in Table 2.

IC is well established as a mature analytical technique, having now been commercialized for over 20 years [7]. The data presented in Table 2 are typical of the performance of modern IC when using carbonate–hydrogencarbonate eluents; i.e., correlation coefficients (r^2) of >0.996 over a three decade concentration range, MDLs at low- $\mu\text{g/l}$ levels, retention time precision of <0.5% RSD, and peak area precision of <1.0% RSD. The routine use of hydroxide as an eluent for inorganic anion analysis has the potential to further improve the performance of IC methods. Hydroxide eluents offer the benefits of improved linearity, lower background conductance and noise when compared to other eluents commonly used for suppressed IC, such as carbonate or tetraborate [8]. The performance of Method 300.0 with an AS17 column and hydroxide gradient produced using an EG40 eluent generator was established by determining method linearity, MDLs, and retention time and peak area precision, which are shown in Table 3.

A comparison of the data in Table 3 with that shown in Table 2 demonstrates the advantages of using hydroxide eluents in IC. Linearity was im-

Table 2
Linearity, MDLs, retention time, and peak area precision obtained for inorganic anions using Method 300.0 with an IonPac AS4A-SC column

Anion ^a	Range (mg/l)	Linearity (r^2)	Calculated MDL ($\mu\text{g/l}$)	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 $\text{NO}_2\text{-N}$)	<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 $\text{NO}_3\text{-N}$)	0.40	0.17
Orthophosphate	0.1–100	0.9967	17.8 (5.8 as $\text{PO}_4\text{-P}$)	0.30	0.35
Sulfate	0.2–200	0.9975	6.7	<0.05	0.14

^a A 50- μl injection was used, as specified in Method 300.0.

Table 3

Linearity, MDLs, retention time, and peak area precision obtained for inorganic anions using Method 300.0 with an IonPac AS17 column

Anion ^a	Range (mg/l)	Linearity (r^2)	Calculated MDL ($\mu\text{g/l}$)	t_R precision (% RSD)	Area precision (% RSD)
Fluoride	0.1–100	0.9996	2.9	0.21	0.18
Chloride	0.2–200	0.9999	2.6	<0.05	0.13
Nitrite	0.1–100	0.9982	3.2 (1.0 as $\text{NO}_2\text{-N}$)	<0.05	0.26
Bromide	0.1–100	0.9993	6.8	0.09	0.23
Nitrate	0.1–100	0.9999	4.2 (1.0 as $\text{NO}_3\text{-N}$)	<0.05	0.19
Orthophosphate	0.1–100	0.9999	12.3 (4.0 as $\text{PO}_4\text{-P}$)	<0.05	0.40
Sulfate	0.2–200	0.9999	5.2	0.07	0.23

^a A 25- μl injection was used.

proved, with correlation coefficients (r^2) of >0.998 over a three decade concentration range, MDLs were approximately 50% lower, despite using a smaller (25 μl) injection volume, retention time precision was $<0.25\%$ RSD, and peak area precision was $<0.5\%$ RSD. The use of the EG40 further enhances method performance by increasing the level of automation of the instrument. No solution other than water is required to operate the system for routine analysis, as the EG40 electrolytically generates the hydroxide eluent, while the ASRS device electrolytically generates the acid used for the suppression reaction.

3.4. Analysis of environmental waters

Once general operating parameters, such as linearity, MDLs, etc., are established, the performance of methods used for environmental analysis are typically validated through single and multi-operator

precision and bias studies on spiked samples. Tables 4 and 5 show single operator recovery results obtained using the IonPac AS4A-SC and AS17 columns for inorganic anions spiked into drinking water, raw (unprocessed drinking) water, and other environmental water matrices. The samples were spiked with the analytes at similar levels to those specified in EPA Method 300.0 [3].

The data in Tables 4 and 5 show that acceptable recoveries (i.e., 80–120%) were obtained for the majority of the inorganic anions, using either column. One exception was the determination of fluoride in the domestic wastewater sample using the AS4A-SC column, where a recovery of $<60\%$ was obtained. In fact, Method 300.0 documents that fluoride concentrations of <1.5 mg/l are subject to interference from mg/l levels of small organic acids, such as formate and acetate, when using the AS4A column. This interference results in high sample fluoride values and lower recoveries for sample

Table 4

Single operator recovery results obtained for inorganic anions spiked in environmental water matrices with Method 300.0 using the IonPac AS4A-SC 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	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 Inappropriate recovery due to microbial action.

Table 5

Single operator recovery results obtained for inorganic anions spiked in environmental water matrices with Method 300.0 using the IonPac AS17 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	115.5	1	109.5	1	110.5	1	103.8	1	119.0	2	110.6
Chloride	10	96.9	20	97.7	40	81.4	20	84.2	20	93.3	5	104.4
Nitrite	2	103.8	2	107.1	4	110.2	2	107.8 ^a	2	96.0	2	111.1
Bromide	2	102.2	2	94.7	2	94.4	2	92.5	2	96.9	2	97.1
Nitrate	5	107.7	5	105.3	10	104.6	5	53.8 ^a	5	108.2	5	102.6
Orthophosphate	10	102.8	10	101.2	10	99.4	20	93.4	20	104.2	20	101.6
Sulfate	20	97.0	40	95.7	40	92.4	40	85.3	40	95.4	20	84.3

^a Inappropriate recovery due to microbial action.

spikes [3]. As such organic acids are likely to be present in a domestic wastewater sample, the lower recovery is not unexpected on the AS4A-SC column, although no interference is observed when using the AS17 column. Also, the recoveries for nitrite and nitrate were not as expected in the domestic wastewater sample, however, at the time of these analyses, the sample had been stored (at 4°C) for longer than the recommended holding time for nitrite/nitrate of 2 days [3]. In this case, the unexpected recoveries were due to the presence of nitrifying–denitrifying microbes in the sample rather than any chromatographic resolution problems.

Fig. 3 shows the chromatograms, on an expanded scale, of a typical low-ionic-strength sample (drinking water) obtained using the IonPac AS4A-SC (a) and AS17 (b) columns, respectively. As the recovery data in Tables 4 and 5 suggest, all peaks are adequately resolved on either column and similar results were obtained for the quantitation of the inorganic anions in the drinking water sample. Fig. 4 shows the chromatograms obtained for a complex, higher-ionic-strength sample (domestic wastewater) when using the IonPac AS4A-SC (a) and AS17 (b) columns, respectively. A large carbonate peak is evident when using the AS17 column (b), although the nitrate peak is still sufficiently resolved for accurate quantitation. The presence of high levels of carbonate (>250 ppm) can cause interference problems when using hydroxide eluents and is a potential disadvantage of this approach. In this instance, somewhat different results are obtained when quan-

titating inorganic anions in the domestic wastewater sample using the different column/eluent combinations. The results obtained for sulfate were lower

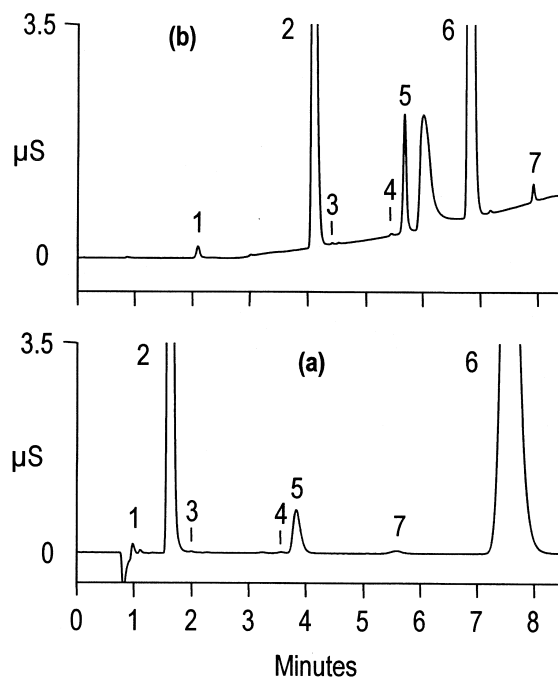


Fig. 3. Analysis of inorganic anions in drinking water. Conditions: as for Fig. 1 except; sample, Sunnyvale, CA, USA tapwater; solutes, (a) 1-fluoride (0.05 mg/l), 2-chloride (21.5 mg/l), 3-nitrite (0.02 mg/l), 4-bromide (0.03 mg/l), 5-nitrate (1.4 mg/l), 6-sulfate (29.7 mg/l), 7-phosphate (0.48 mg/l); (b) 1-fluoride (0.06 mg/l), 2-chloride (24.1 mg/l), 3-nitrite (0.01 mg/l), 4-bromide (0.02 mg/l), 5-nitrate (1.5 mg/l), 6-sulfate (31.4 mg/l), 7-phosphate (0.28 mg/l).

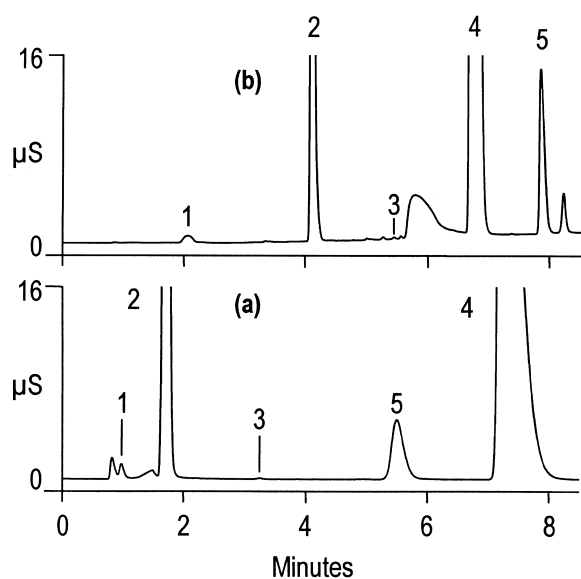


Fig. 4. Analysis of inorganic anions in domestic wastewater. Conditions: as for Fig. 1 except; sample, domestic wastewater from a septic tank; solutes, (a) 1-fluoride (0.46 mg/l), 2-chloride (67.9 mg/l), 3-bromide (0.12 mg/l), 4-sulfate (155 mg/l), 5-phosphate (29.9 mg/l); (b) 1-fluoride (0.41 mg/l), 2-chloride (66.7 mg/l), 3-bromide (0.13 mg/l), 4-sulfate (181 mg/l), 5-phosphate (28.7 mg/l).

(155 mg/l) when using the AS4A-SC column and carbonate–hydrogencarbonate eluent compared to those obtained using the AS17 column (181 mg/l). This was due to the fact that calibration curves are not strictly linear with suppressed conductivity detection when using carbonate-based eluents, hence the amount of sulfate was under-estimated at the relatively high concentration present in the sample. In fact, Method 300.0 recommends an upper calibration range of 95 mg/l for sulfate and diluting the sample into the working range if the concentration exceeds 95 mg/l [3]. Therefore, the improved linearity offered by the use of hydroxide eluents can improve sample throughput by reducing the need to dilute and re-run higher ionic strength samples.

3.5. PBMS tier 1 method validation

The use of an hydroxide eluent and optional column is considered a modification of Method 300.0 under the EPA Office of Water Performance Based Measurement System (PBMS) guidelines [9].

Under the new PBMS initiative, the Office of Water is combining wastewater and drinking water programs to implement a method approval program that will expand method flexibility and expedite approval of new methods. It is intended that PBMS will promote new technologies and facilitate faster approval of new methods at 40 CFR parts 136 (wastewater) and 141 (drinking water). In turn, the new technologies are expected to enhance data quality, reduce laboratory waste, and lower measurement costs.

PBMS is introducing three “Tiers” of method validation. Tier 1 is for a single laboratory seeking approval for one (or more) matrix types. In this case, validation and a certification statement will be required, although EPA approval is not required. Tier 2 is for all laboratories seeking approval for one (or more) matrix types. In this case, validation and a certification statement will be required, and EPA approval is now required. Tier 3 is for all laboratories seeking approval for all matrix types. In this case, validation and a certification statement will be required, and EPA approval is again required.

Tier 1 validation requires a demonstration of initial precision and recovery (IPR) using the reference method (i.e., Method 300.0) and modified method to demonstrate the laboratory can practice both methods. An IPR demonstration is not required with the reference method if the laboratory is currently using that method. The IPR modified method validation requires the analysis of: (a) four replicates of reagent water spiked with analytes of interest, (b) a blank, (c) matrix spike/matrix spike duplicate, and (d) seven replicates of an MDL standard. The reagent water and matrix must be spiked with analytes of interest at the level specified in the reference method. Four replicates of the matrix spike must be run for a new method, as opposed to two for a modified method [9].

The results of the IPR study are then used to establish quality control acceptance criteria for the modified method, all of which must meet the criteria of the reference method. In reality, the PBMS Tier 1 validation is a program showing a wide demonstration of proficiency very similar to the initial demonstration of performance required specifically for Method 300.0. Tables 6 and 7 show the results obtained for four spiked reagent water and drinking

Table 6

Tier 1 modified method IPR results and quality control acceptance criteria obtained for inorganic anions in four spiked reagent water samples

Anion	Amount added ^a (mg/l)	Mean recovery (%)	Precision (%)	QC criteria precision ^b (%)	QC criteria lower recovery limit (%)	QC criteria upper recovery limit (%)
Fluoride	2	102.2	3.2	9.5	92.7	111.7
Chloride	20	86.7	0.6	9.5	77.2	96.1
Nitrite	10	95.8	1.4	9.5	86.4	105.3
Bromide	5	91.5	0.8	9.5	82.0	101.0
Nitrate	10	98.1	0.4	9.5	88.6	107.6
Orthophosphate	10	94.2	0.5	9.5	84.7	103.6
Sulfate	20	86.5	0.1	9.5	77.1	96.0

^a Amount specified in Method 300.0.

^b QC criteria=3×largest σ value.

water samples using the AS17 column and an hydroxide gradient. In all cases, acceptable recoveries were obtained for anions spiked in both matrices, while the quality control acceptance criteria are within the acceptable ranges defined by Method 300.0.

4. Conclusions

The use of ion chromatography with an IonPac AS17 column, EG40 eluent generator, and potassium hydroxide gradient represents a new approach to the routine determination of inorganic anions in environmental waters. This approach is a modification

of EPA Method 300.0, which allows equivalent method performance with improved linearity, precision, and MDLs. The AS17 column provides superior retention of fluoride from the column void volume and improved resolution from small organic acids, such as formate and acetate, compared to the AS4A column specified in Method 300.0. Quantitative recoveries were obtained for all common inorganic anions spiked into typical environmental waters using this new approach, and the PBMS Tier 1 method validation quality control acceptance criteria are well within the acceptable ranges defined by Method 300.0. In addition, the EG40 eluent generator eliminates the need to manually prepare eluents, increasing the level of automation and ease-of-use of the IC system.

Table 7

Tier 1 modified method IPR results and quality control acceptance criteria obtained for inorganic anions in four spiked drinking water samples

Anion	Amount added ^a (mg/l)	Mean recovery (%)	Precision (%)	QC criteria precision ^b (%)	QC criteria lower recovery limit (%)	QC criteria upper recovery limit (%)
Fluoride	1	107.6	2.6	7.9	99.7	115.5
Chloride	20	80.5	0.7	7.9	72.6	88.4
Nitrite	10	95.7	1.3	7.9	87.8	103.6
Bromide	5	93.5	0.5	7.9	85.6	101.4
Nitrate	10	97.7	1.0	7.9	89.8	105.6
Orthophosphate	10	95.9	0.4	7.9	88.0	103.8
Sulfate	50	84.4	0.4	7.9	76.5	92.3

^a Amount specified in Method 300.0.

^b QC criteria=3×largest σ value.

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