DIONEX

Application Note 135

Determination of Inorganic Anions in Wastewater by Ion Chromatography

INTRODUCTION

The determination of common inorganic anions in environmental waters, such as wastewater and drinking, ground, and surface waters, is one of the most important applications of ion chromatography (IC) worldwide. Water quality in the U.S. is legislated through the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA). The SDWA ensures the integrity and saftey of U.S. drinking water, and the goal of the CWA is to reduce the discharge of pollutants into U.S. waters.[1,2] Ion chromatography has been approved for compliance monitoring of these common inorganic anions in U.S. drinking water since the mid-1980s, as described in U.S. EPA Method 300.0.[3] This method received technical approval in 1992 and interim regulatory approval in 1995 for the analysis of inorganic anions in wastewater under the National Pollution Discharge Elimination System (NPDES) permits program.[2]

Many other industrialized countries have similar health and environmental standards and a considerable number of regulatory IC methods have been published worldwide (e.g., in Germany, France, Italy, and Japan) for the determiniation of anions in wastewater. In addition, many standards organizations (including ISO, ASTM, and AWWA) have validated IC methods for the analysis of inorganic anions in wastewater.[4,5] This Application Note describes the determination of inorganic anions in wastewater and other environmental waters using conditions that are consistent with those in U.S. EPA Method 300.0.[3] The use of two optional columns, the IonPac® AS14 and IonPac AS9-HC, is also discussed.

EQUIPMENT

Dionex DX-120 and DX-500 Ion Chromatography Systems were used for this work. The DX-120 is a dedicated ion chromatograph; the DX-500 is a modular system, which in this case consisted of:

GP50 Gradient Pump

CD20 Conductivity Detector

AD20 UV/Vis Detector

LC20 Chromatography Enclosure with rear-loading injection valve

AS40 Automated Samplers (5-mL vials) and a

PeakNet™ Chromatography Workstation were used with both systems.

REAGENTS AND STANDARDS

Deionized water, Type I reagent grade, 18 MΩ-cm resistance or better

0.18 M Sodium carbonate/0.17 M Sodium bicarbonate (Dionex IonPac AS4A Eluent Concentrate, P/N 39513)

0.35 M Sodium carbonate/0.1 M Sodium bicarbonate (Dionex IonPac AS14 Eluent Concentrate, P/N 53560)

0.5 M Sodium carbonate (Dionex P/N 37162)

Sodium and potassium salts, ACS reagent grade, for preparing anion standards (VWR or other)

Fluoride standard 1000 mg/L, 100 mL (Dionex P/N 37158)

Chloride standard 1000 mg/L, 100 mL (Dionex P/N 37159)

Sulfate standard 1000 mg/L, 100 mL (Dionex P/N 37160)

Nitrate standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-004)

Nitrite standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-007)

Phosphate standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-005)

Bromide standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-001)

CONDITIONS

Part A

Columns:	IonPac AG4A-SC, 4 x 50 mm (P/N 43175) IonPac AS4A-SC, 4 x 250 mm (P/N 43174)
Eluent:	1.8 mM Sodium carbonate/ 1.7 mM Sodium bicarbonate
Run Time:	< 8 min
Flow Rate:	2.0 mL/min
Injection Volume:	50 µL
Detection:	Suppressed conductivity, ASRS®-ULTRA (4 mm) in recycle mode, 50 mA current
System Backpressure:	~ 1000 psi
Background Conductance:	~ 14 µS

Part B

Columns:	IonPac AG14, 4 x 50 mm (P/N 46134) IonPac AS14, 4 x 250 mm (P/N 46124)
Eluent:	3.5 mM Sodium carbonate/ 1.0 mM Sodium bicarbonate
Run Time:	< 14 min
Flow Rate:	1.2 mL/min
Injection Volume:	50 µL
Detection:	Suppressed conductivity, ASRS-ULTRA (4 mm) in recycle mode, 100 mA current
System Backpressure:	~ 1600 psi
Background Conductance:	~ 17 µS

Part C

Columns:	IonPac AG9-HC, 4 x 50 mm (P/N 51761) IonPac AS9-HC, 4 x 250 mm (P/N 51786)
Eluent:	9.0 mM Sodium carbonate
Run Time:	< 24 min
Flow Rate:	1.0 mL/min
Injection Volume:	50 µL
Detection:	Suppressed conductivity, ASRS-ULTRA (4 mm) in recycle mode, 100 mA current
System Backpressure:	~ 2200 psi
Background Conductance:	~ 22 µS

PREPARATION OF SOLUTIONS AND REAGENTS

Stock Standard Solutions

Stock Anion Standard Solutions (1000 mg/L)

For several of the analytes of interest, 1000 mg/L standard solutions are available from Dionex and other commercial sources. When commercial standards are not available, 1000 mg/L standards can be prepared by dissolving the appropriate amounts of the corresponding mass in 1000 mL of deionized water according to Table 1. Standards are stable for at least one month when stored at 4 °C.

Table 1 Masses of Compounds Used to Prepare 1 L of 1000 mg/L Anion Standards

Anion	Compound	Mass (g)
Fluoride	Sodium fluoride (NaF)	2.210
Chloride	Sodium chloride (NaCl)	1.648
Nitrite	Sodium nitrite ($NaNO_2$)	1.499
Bromide	Sodium bromide (NaBr)	1.288
Nitrate	Sodium nitrate ($NaNO_3$)	1.371
o-Phosphate	Potassium phosphate, monobasic (KH_2PO_4)	1.433
Sulfate	Sodium sulfate (Na_2SO_4)	1.522

Table 2 Concentration of Linearity, MDL, and Reproducibility Standards

Anion	Seven-Point Calibration Range (mg/L)	MDL Calculation Standard (mg/L)	QCS Standard for RSD Calculation (mg/L)
Fluoride	0.1–100	0.025	2
Chloride	0.2–200	0.010	20
Nitrite	0.1–100	0.025	2
Bromide	0.1–100	0.050	2
Nitrate	0.1–100	0.045	10
o-Phosphate	0.1–100	0.045	2
Sulfate	0.2–200	0.050	60

Working Standard Solutions

Composite working standards at lower analyte concentrations are prepared from the 1000 mg/L standards described above. Working standards containing less than 100 mg/L anions should be prepared daily. Table 2 shows the linear concentration range investigated for each anion, as well as the concentration of the standard used to calculate the method detection limits (MDLs) and the concentration of the quality control sample (QCS) used to determine the retention time and peak area precision.

Eluent Solutions

For the IonPac AS4A-SC and AS14 columns, dilute 20 mL of the appropriate eluent concentrate to 2.0 L with deionized water. For the IonPac AS9-HC column, dilute 36 mL of the 0.5 M sodium carbonate concentrate to 2.0 L with deionized water. Transfer to a 2-L eluent container and pressurize the container with helium at 8 psi.

SAMPLE PREPARATION

All samples were filtered through appropriate 0.45-µm syringe filters, discarding the first 300 µL of the effluent to waste, as specified in Section 4.4 of EPA Method 300.0.[3] The domestic wastewater sample was treated with a C_{18} Sep-Pak cartridge to remove hydrophobic organic material in order to prolong column lifetimes.[6] The C_{18} cartridge was preconditioned with 5 mL of methanol followed by 5 mL of deionized water. The sample (5 mL) was then passed through the cartridge, with the first 1 mL of the effluent being discarded. Aqueous soil extracts were prepared by the extraction of 3.0 g of soil in 30 mL of deionized water in an ultrasonic bath for 30 min followed by filtration with a 0.45-µm filter.

RESULTS AND DISCUSSION

A variety of methods have been used for the analysis of inorganic anions, including traditional spectroscopic techniques such as colorimetry; wet chemical methods such as gravimetric analysis, turbidimetry, and titrimetry; and electrochemical techniques such as ion selective electrodes (ISEs) and amperometric titrations.[4] However, many of these methods are not specific and suffer from interferences or limited sensitivity; they also can be labor-intensive and are often difficult to automate. Because many of the individual test procedures described above can be replaced by one chromatographic separation, IC was quickly accepted by regulatory agencies worldwide for the determination of anions in wastewater and other environmental waters.

IonPac AS4A-SC Column

U.S. 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 bicarbonate for the separation of common anions.[3] The method specifies the use of an AMMS® (Anion MicroMembrane Suppressor) operated in the chemical regeneration mode; however, an ASRS (Anion Self-Regenerating Suppressor) provides equivalent method performance with added convenience. Conductivity is used as a bulk property detector for the measurement of inorganic anions.

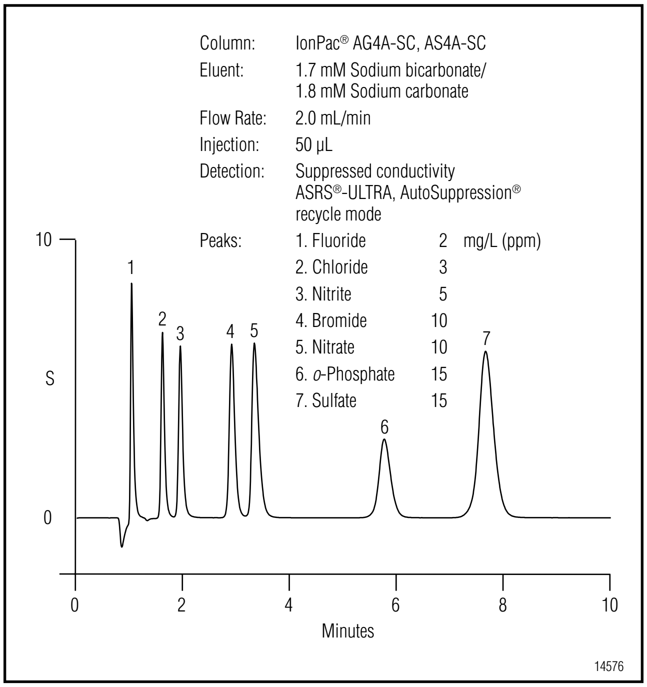


Figure 1. Separation of a low-ppm inorganic anion standard using an IonPac AS4A-SC column.

Figure 1 shows a typical chromatogram of a standard containing low-ppm levels of common inorganic anions separated using an IonPac AS4A-SC column as described in Part A of the "Conditions" section. The pellicular AS4A-SC column has an outer layer of latex with selectivity similar to that of the AS4A, 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 well resolved within a total run time of less than 8 min. The method linearity was determined for the inorganic anions over a seven-point calibration range. MDLs were calculated for each of the anions according to the procedure described in U.S. EPA Method 300.0.[3] The MDLs are estimated by injecting seven replicates of reagent water fortified at a concentration of 3 to 5 times the estimated instrument detection limit. The MDL is then calculated as (t) x (SD) where t = Student's t value for a 99% confidence level and a standard deviation estimate with n - 1 degrees of freedom (t = 3.14 for seven replicates) and SD = standard deviation of the replicate analysis.

Table 3 shows the concentration ranges investigated, the resulting linear coefficients of determination (r^2), and the calculated MDL for each anion. The retention time and peak area precision (expressed as % RSD) were determined from seven replicate injections of a quality control sample, as described in Table 2. Table 3 also shows typical retention time and peak area precision data that can be obtained for inorganic anions using the IonPac AS4A-SC column with a DX-120 system.

Table 3 Linearity, MDL, Retention Time, and Peak Area Precision Obtained Using the IonPac AS4A-SC Column[a]

Anion	Range (mg/L)	Linearity (r^2)	Calculated MDL[b] (µg/L)	Retention Time Precision (% RSD[c])	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%
o-Phosphate	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] Dionex DX-120 system

[b] MDL = $\sigma^* t_{s,99}$ where $t_{s,99}$ = 3.14 for n = 7

[c] RSD = Relative standard deviation, n = 7

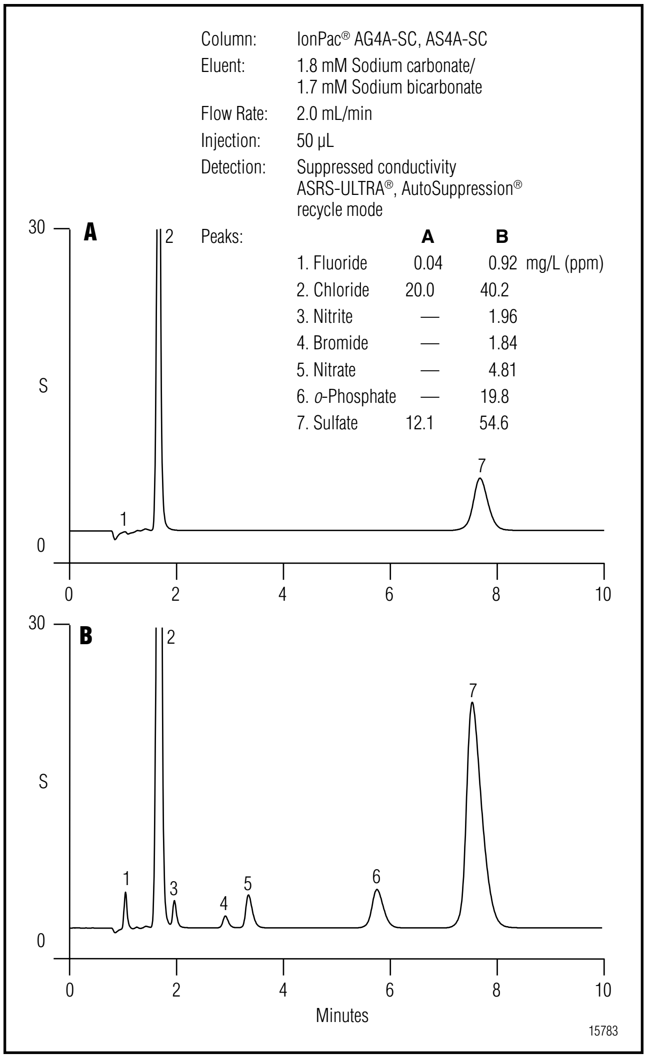
The performance of methods used for environmental analysis are typically validated through single- and multi-operator precision and bias studies on spiked samples. Table 4 shows typical recovery results for single-operator data obtained using the IonPac AS4A-SC column for common anions spiked into industrial wastewater, domestic wastewater, and other environmental water matrices. The samples were spiked with the analytes at approximately the same levels as specified in U.S. EPA Method 300.0.[3]

Table 4 Anion Recoveries for Spiked Water Samples Obtained Using the IonPac AS4A-SC Column

Anion	Drinking Water		Raw Water		Surface Water	
	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)
Fluoride	1	93.9	1	96.5	1	109.0
Chloride	10	97.4	20	83.2	40	81.4
Nitrite	2	91.6	2	102.1	4	105.0
Bromide	2	98.7	2	96.7	2	101.0
Nitrate	5	92.4	5	94.4	10	96.7
o-Phosphate	10	95.0	10	95.4	10	107.9
Sulfate	20	97.5	40	106.8	40	106.4
Anion	**Domestic Wastewater**		**Industrial Wastewater**		**Soil Extract**	
	Amt. Added (mg/L)	**Recovery (%)**	**Amt. Added (mg/L)**	**Recovery (%)**	**Amt. Added (mg/L)**	**Recovery (%)**
Fluoride	1	57.0	1	88.0	2	99.0
Chloride	20	82.7	20	100.8	5	100.2
Nitrite	2	217.0*	2	98.0	2	102.5
Bromide	2	86.5	2	92.0	2	91.0
Nitrate	5	6.8*	5	96.2	5	90.2
o-Phosphate	20	101.6	20	98.8	20	111.7
Sulfate	40	90.6	40	105.9	20	96.6

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

Figure 2A shows a chromatogram of inorganic anions in industrial wastewater from a chemical manufacturing plant obtained using the IonPac AS4A-SC column. Figure 2B shows the same wastewater sample spiked with 1–40 mg/L of inorganic anions. All peaks are well resolved in the spiked sample and acceptable recoveries (i.e., 80–120%) were obtained for all anions in this relatively simple matrix. Figure 3 shows a chromatogram of inorganic anions in a more complex matrix, domestic wastewater from a septic sewage system. In general, Table 4 shows that acceptable recovery data was obtained for the inorganic anions in most matrices.



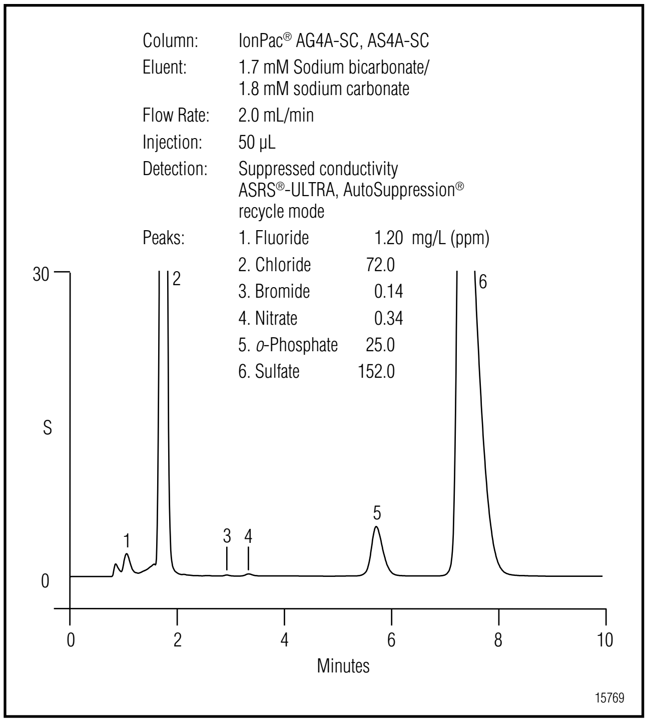
Column: IonPac® AG4A-SC, AS4A-SC
Eluent: 1.8 mM Sodium carbonate/ 1.7 mM Sodium bicarbonate
Flow Rate: 2.0 mL/min
Injection: 50 µL
Detection: Suppressed conductivity ASRS-ULTRA®, AutoSuppression® recycle mode

Peaks:	A	B	
1. Fluoride	0.04	0.92	mg/L (ppm)
2. Chloride	20.0	40.2	
3. Nitrite	—	1.96	
4. Bromide	—	1.84	
5. Nitrate	—	4.81	
6. *o*-Phosphate	—	19.8	
7. Sulfate	12.1	54.6	

Figure 2. Determination of inorganic anions in A) industrial wastewater and B) spiked industrial wastewater using an IonPac AS4A-SC column.

The one exception was the domestic wastewater sample, shown in Figure 3, where a recovery of < 60% was obtained for fluoride under these conditions. 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.[3] Consequently, this column is not recommended for the analysis of fluoride in complex samples that contain small organic acids.

In this sample, the recoveries for nitrite and nitrate were also not as expected. At the time of these analyses, the sample had been stored (at 4 °C) for longer that the two-day recommended holding time for nitrite/nitrate.[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.



Column: IonPac® AG4A-SC, AS4A-SC
Eluent: 1.7 mM Sodium bicarbonate/ 1.8 mM sodium carbonate
Flow Rate: 2.0 mL/min
Injection: 50 µL
Detection: Suppressed conductivity ASRS®-ULTRA, AutoSuppression® recycle mode

Peaks:	
1. Fluoride	1.20 mg/L (ppm)
2. Chloride	72.0
3. Bromide	0.14
4. Nitrate	0.34
5. *o*-Phosphate	25.0
6. Sulfate	152.0

Figure 3. Determination of anions in domestic wastewater using an IonPac AS4A-SC column.

IonPac AS14 Column

While U.S. EPA Method 300.0 specifies the use of an IonPac AS4A column, Section 6.2.2.1 states that “an optional column may be used if comparable resolution of peaks is obtained and the quality control requirements of Section 9.2 can be met.” The IonPac AS14 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 column provides complete resolution of fluoride from formate and acetate in addition to improved resolution of fluoride from the column void peak.

The improved selectivity and higher capacity of the AS14 column (65 µeq/column compared to 20 µeq/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 lower peak efficiencies than those obtained using the latex-agglomerated AS4A-SC column. Figure 4 shows a typical chromatogram of a standard containing low-ppm levels of common anions separated using the IonPac AS14 column as described in Part B of the “Conditions” section. Fluoride is clearly resolved from the column void volume and the overall selectivity is improved compared to the chromatogram shown in Figure 1, although the total run time is increased to 14 min.

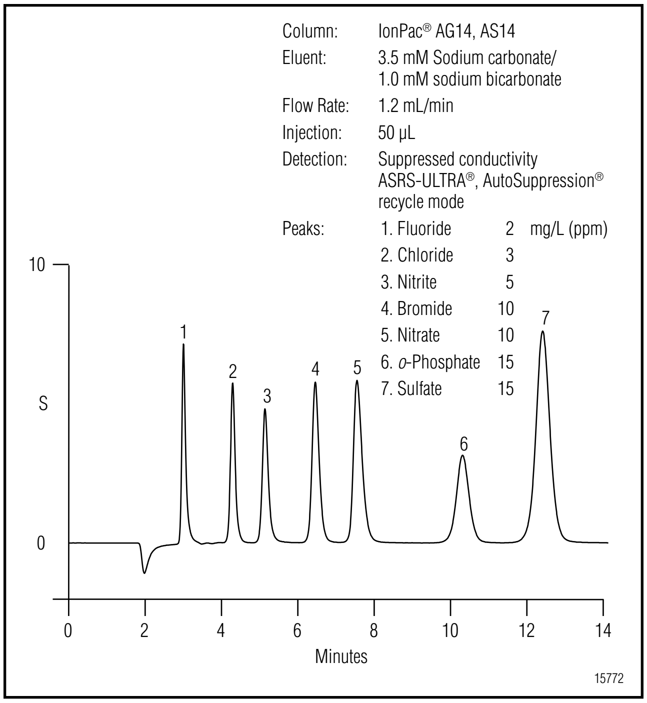


Figure 4. Separation of a low-ppm inorganic anion standard using an IonPac AS14 column.

The method linearity using the AS14 column was again determined over a seven-point calibration range and the MDLs were calculated according to U.S. EPA Method 300.0.[3] Table 5 shows the concentration ranges investigated, the resulting linear coefficients 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 the quality control sample. Table 5 also shows typical retention time and peak area precision data that can be obtained for inorganic anions using the IonPac AS14 column with a DX-500 system. The performance of the AS14 method was also validated through single-operator precision and bias studies on spiked samples. Table 6 shows typical recovery results for single-operator data obtained using the IonPac AS14 column for common anions spiked into industrial wastewater, domestic wastewater, and other environmental water matrices.

Table 5 Linearity, MDL, Retention Time, and Peak Area Precision Obtained Using the IonPac AS14 Column[a]

Anion	Range (mg/L)	Linearity (r^2)	Calculated MDL[b] (µg/L)	Retention Time Precision (% RSD[c])	Area Precision (% RSD)
Fluoride	0.1–100	0.9980	3.5	0.23%	0.17%
Chloride	0.2–200	0.9995	2.9	0.41%	0.51%
Nitrite	0.1–100	0.9997	6.5 (2.0 as NO_2-N)	0.40%	0.37%
Bromide	0.1–100	0.9976	7.8	0.56%	0.51%
Nitrate	0.1–100	0.9970	7.7 (1.7 as NO_3-N)	0.66%	0.54%
o-Phosphate	0.1–100	0.9963	20.2 (6.6 as PO_4-P)	0.15%	0.57%
Sulfate	0.2–200	0.9973	8.2	0.15%	0.59%

[a] Dionex DX-500 system

[b] MDL = $\sigma^* t_{s,99}$ where $t_{s,99}$ = 3.14 for n = 7

[c] RSD = Relative standard deviation, n = 7

Table 6 Anion Recoveries for Spiked Water Samples Obtained Using the IonPac AS14 Column

Anion	Drinking Water		Raw Water		Surface Water	
	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)
Fluoride	1	91.5	1	85.1	1	101.0
Chloride	10	94.6	20	84.0	40	83.6
Nitrite	2	103.1	2	92.0	4	100.2
Bromide	2	96.1	2	95.6	2	93.3
Nitrate	5	87.2	5	89.4	10	93.2
o-Phosphate	10	93.8	10	94.2	10	106.4
Sulfate	20	96.1	40	106.6	40	106.1

Anion	Domestic Wastewater		Industrial Wastewater		Soil Extract	
	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)
Fluoride	1	90.8	1	90.1	2	101.1
Chloride	20	87.3	20	96.7	5	96.7
Nitrite	2	0.0*	2	98.2	2	89.3
Bromide	2	96.8	2	96.2	2	89.9
Nitrate	5	15.3*	5	95.1	5	92.8
o-Phosphate	20	94.3	20	95.9	20	111.0
Sulfate	40	91.5	40	102.0	20	94.7

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

Figure 5 shows a chromatogram of inorganic anions in the same domestic wastewater sample shown in Figure 3, obtained using the IonPac AS14 column. In this case, fluoride clearly is well resolved from the column void volume and also from the later eluting (acetate) peak. Table 6 shows that acceptable recovery data (i.e., 80–120%) was obtained for the inorganic anions in all matrices when using the AS14 column, with the exception of nitrite and nitrate in the same domestic wastewater sample. However, this was again due to the presence of nitrifying/denitrifying microbes rather than any chromatographic resolution problems, although the sample had now been held for a different length of time than when the analysis was first performed using the AS4A-SC column.

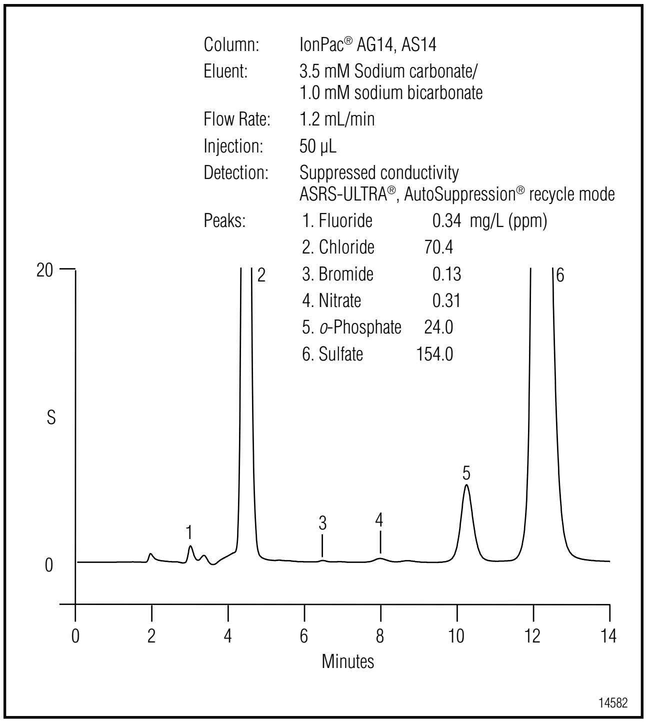


Figure 5. Determination of inorganic anions in domestic wastewater using an IonPac AS14 column.

IonPac AS9-HC Column

The IonPac AS14 column provides suitable performance for the determination of anions in the majority of wastewater samples; however, very high ionic strength wastewaters are best analyzed using a still higher capacity column. The pellicular stationary phases typically used in IC have a monolayer of fully functionalized latex particles that are electrostatically attached to a surface-functionalized, microporous core particle. The ion-exchange capacity of the resin can be increased by using a larger diameter latex, although this approach ultimately results in decreased efficiency when producing high capacity columns.[7] The AS9-HC column uses a superporous (2000-Å pore size) resin consisting of EVB crosslinked with 55% DVB. This core particle allows the methacrylate-based latex layer to be thinly coated on both the exterior and interior surfaces of the resin and provides a simple way to produce a column with higher capacity (190 µeq/column) using a standard diameter latex while maintaining high chromatographic efficiency.[8]

Figure 6 shows a typical chromatogram of a standard containing low-ppm levels of common anions separated using the IonPac AS9-HC column as described in Part C of the “Conditions” section. Fluoride is again clearly resolved from the void volume and the overall peak resolution is further improved compared to both the AS4A-SC and AS14 columns, hence the AS9-HC column is ideal for the analysis of samples containing dissimilar levels of inorganic anions. The disadvantages of using the high capacity AS9-HC column are that the total run time increases to 24 min and the peak response is reduced when compared to that obtained using the lower capacity AS4A-SC and AS14 columns.

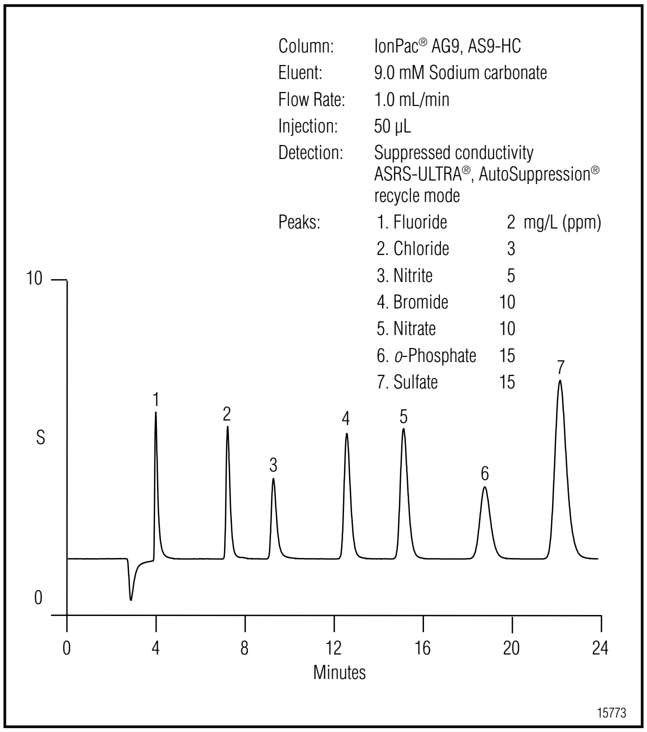


Figure 6. Separation of a low-ppm inorganic anion standard using an IonPac AS9-HC column.

The method linearity using the AS9-HC column was again determined over a seven-point calibration range and the MDLs were calculated according to U.S. EPA Method 300.0.[3] Table 7 shows the concentration ranges investigated, the resulting linear coefficients 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 the quality control sample. Table 7 also shows typical retention time and peak area precision data that can be obtained for inorganic anions using the IonPac AS9-HC column with a DX-500 system.

Table 7 Linearity, MDL, Retention Time, and Peak Area Precision Obtained Using the IonPac AS9-HC Column[a]

Anion	Range (mg/L)	Linearity (r^2)	Calculated MDL[b] (µg/L)	Retention Time Precision (% RSD[c])	Area Precision (% RSD)
Fluoride	0.1–100	0.9980	7.4	0.36%	0.58%
Chloride	0.2–200	0.9989	5.4	0.22%	0.27%
Nitrite	0.1–100	0.9994	6.2 (1.9 as NO_2-N)	< 0.05%	0.74%
Bromide	0.1–100	0.9968	12.1	0.12%	0.56%
Nitrate	0.1–100	0.9962	10.7 (2.4 as NO_3-N)	0.13%	0.23%
o-Phosphate	0.1–100	0.9972	31.1 (10.2 as PO_4-P)	0.08%	0.75%
Sulfate	0.2–200	0.9967	14.4	0.08%	

[a] Dionex DX-500 system
[b] MDL = $\sigma * t_{s,99}$ where $t_{s,99} = 3.14$ for n = 7
[c] RSD = Relative standard deviation, n = 7

The performance of the AS9-HC method was also validated through single-operator precision and bias studies on spiked samples. Table 8 shows typical recovery results for single-operator data obtained using the IonPac AS9-HC column for common anions spiked into industrial wastewater, domestic wastewater, and other environmental water matrices. Table 8 shows that acceptable recovery data (i.e., 80–120%) was also obtained for the inorganic anions in all matrices when using the AS9-HC column.

Table 8 Anion Recoveries for Spiked Water Samples Obtained Using the IonPac AS9-HC Column

Anion	Drinking Water		Raw Water		Surface Water	
	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)
Fluoride	1	94.8	1	93.3	1	108.3
Chloride	10	96.3	20	85.1	40	81.4
Nitrite	2	95.5	2	96.5	4	106.9
Bromide	2	94.4	2	94.0	2	99.4
Nitrate	5	118.1	15	85.6	10	99.0
o-Phosphate	10	97.4	10	101.9	10	102.1
Sulfate	20	101.9	40	113.2	40	108.9

Anion	Domestic Wastewater		Industrial Wastewater		Soil Extract	
	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)
Fluoride	1	106.8	1	103.6	1	82.5
Chloride	20	86.7	20	104.6	50	86.1
Nitrite	2	102.6	2	103.1	5	118.1
Bromide	2	99.6	2	99.3	2	100.6
Nitrate	5	100.8	5	101.6	5	118.5
o-Phosphate	20	103.5	20	104.9	10	84.3
Sulfate	40	81.4	40	107.5	40	110.5

Figure 7 shows a chromatogram of 0.2 ppm nitrite spiked into ASTM substitute wastewater (which had been modified to contain elevated levels of chloride and lower nitrite levels) obtained with the AS9-HC column and dual detection using suppressed conductivity and UV/Vis absorption at 214 nm.[9] These chromatograms show the benefit of increased column capacity as chloride and nitrite can be determined at ratios up to 10,000:1 with the AS9-HC column when using conductivity detection. The use of direct UV detection at 214 nm is selective for UV-absorbing anions such as nitrite, bromide, and nitrate and allows the determination of nitrite in the presence of still higher levels of chloride. Table 9 shows the maximum chloride:nitrite ratios that can be analyzed with the AS14 and AS9-HC columns using conductivity and direct UV detection. Note that the ratio is stated with nitrite expressed as both NO_2 and NO_2-N.

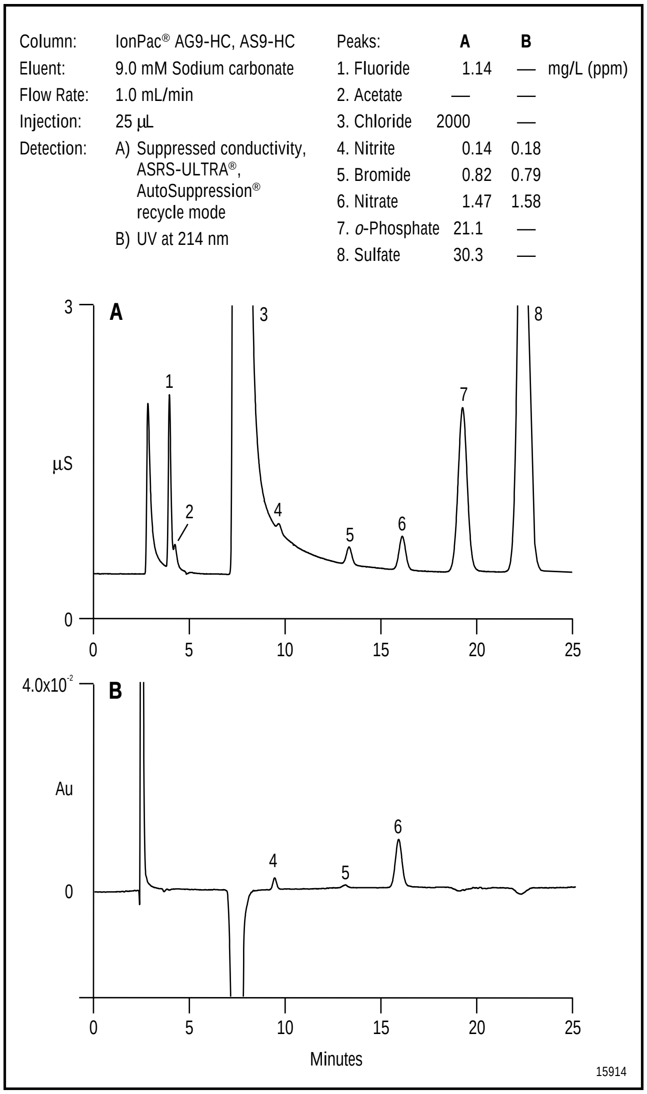


Figure 7. Determination of low levels of nitrite in wastewater containing elevated levels of chloride using the AS9-HC column with dual A) suppressed conductivity and B) UV/Vis detection.

Table 9 Maximum Cl:NO_2 Ratios at Which Nitrite Can Be Quantified Using the IonPac AS14 and AS9-HC Columns[a]

Column and Detection Mode	Cl:NO_2	Cl:NO_2-N
AS14; Conductivity	100:0.1 mg/L (1,000:1)	100:0.034 mg/L (3285:1)
AS14; UV (214 nm)	500:0.03 mg/L (16,667:1)	500:0.009 mg/L (54,761:1)
AS9-HC; Conductivity	2000:0.2 mg/L (10,000:1)	2000:0.068 mg/L (32,850:1)
AS9-HC; UV (214 nm)	5000:0.045 mg/L (111,000:1)	5000:0.014 mg/L (365,000:1)

[a] Dionex DX-500 system with a 25-µL injection

SUMMARY

The IonPac AS4A-SC column provides suitable performance for the determination of inorganic anions in low ionic strength wastewater samples and similar matrices, such as drinking, raw, and surface waters, as outlined in U.S. EPA Method 300.0. Low levels of fluoride are subject to interference from mg/L levels of small organic acids with the AS4A column, hence this column is not recommended for the analysis of fluoride in more complex wastewater samples that may contain small organic acids.

The IonPac AS14 column provides improved fluoride resolution from the column void peak and complete resolution of fluoride from formate and acetate. The improved selectivity and higher capacity make the AS14 column the most appropriate choice for the routine determination of inorganic anions in typical, moderate ionic strength domestic and industrial wastewater samples. The IonPac AS9-HC column has a significantly higher capacity than the AS4A-SC and AS14 columns, so total run times are longer and peak response is somewhat reduced; however, this column is ideal for the determination of inorganic anions in high ionic strength wastewater samples. This column can be used to determine nitrite in a 10,000-fold excess of chloride when using conductivity detection, while direct UV detection allows the determination of nitrite in the presence of still higher levels of chloride.

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