Determination of Inorganic Anions in Drinking Water by Ion Chromatography

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Introduction

The determination of common inorganic anions in drinking water is one of the most important applications of ion chromatography (IC) worldwide. The National Primary Drinking Water Standards in the United States 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 the ingestion of these anions in drinking water.[1] High levels of fluoride cause skeletal and dental fluorosis, and nitrite and nitrate can cause methemoglobulinemia, which can be fatal to infants. Other common anions, such as chloride and sulfate, are considered secondary contaminants. The National Secondary Drinking Water Standards in the U.S. are guidelines regarding taste, odor, color, and certain aesthetic characteristics. Although these guidelines are not federally enforced, they are recommended to all states as reasonable goals and many states adopt their own regulations governing these contaminants.[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] 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 analysis of anions in drinking water. In addition, many standards organizations (including ISO, ASTM, and AWWA) have validated IC methods for the analysis of inorganic anions in drinking water.[4,5]

This application note describes the determination of inorganic anions in drinking water and other environmental waters using conditions that are consistent with those in U.S. EPA Method 300.0.3 The use of an optional column, the Thermo Scientific Dionex™ IonPac™ AS14 column, is also discussed.

Equipment

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

- Thermo Scientific Dionex GP50 Gradient Pump
- Thermo Scientific Dionex CD20 Conductivity Detector
- Thermo Scientific Dionex LC20 Chromatography Enclosure with rear-loading injection valve
- Thermo Scientific Dionex AS40 Automated Samplers (5 mL vials) and a Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstations 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
- 0.35 M Sodium carbonate/0.1 M Sodium bicarbonate: Dionex IonPac AS14 Eluent Concentrate
- Sodium and Potassium salts, ACS reagent grade, for preparing anion standards
- Fluoride standard 1000 mg/L, 100 mL
- Chloride standard 1000 mg/L, 100 mL
- Sulfate standard 1000 mg/L, 100 mL
- Nitrate standard 1000 mg/L, 100 mL
- Phosphate standard 1000 mg/L, 100 mL
- Bromide standard 1000 mg/L, 100 mL

Conditions

Part A

Columns:	Dionex IonPac AG4A-SC, 4 × 50 mm Dionex IonPac AS4A-SC, 4 × 250 mm
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, Thermo Scientific™ Dionex™ ASRS™ ULTRA Anion Self-Regenerating suppressor (4 mm), recycle mode, 50 mA current
System Backpressure:	~1000 psi
Background Conductance:	~14 µS

Part B

Columns:	Dionex IonPac AG14, 4 × 50 mm Dionex IonPac AS14, 4 × 250 mm
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, Dionex ASRS ULTRA suppressor (4 mm), recycle mode, 100 mA current
System Backpressure:	~1600 psi
Background Conductance:	~17 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 Thermo Scientific 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)	1.479

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.

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

Eluent Solutions

Dilute 20 mL of the appropriate eluent 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

The vial caps in the Thermo Scientific Dionex AS40 Automated Sampler contain a 20 µm filter, so no additional filtration was used in conjunction with this mode of sample introduction. If a Dionex AS40 is not used, filter all samples through appropriate 0.45 µm syringe filters, discarding the first 300 µL of the effluent. 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.

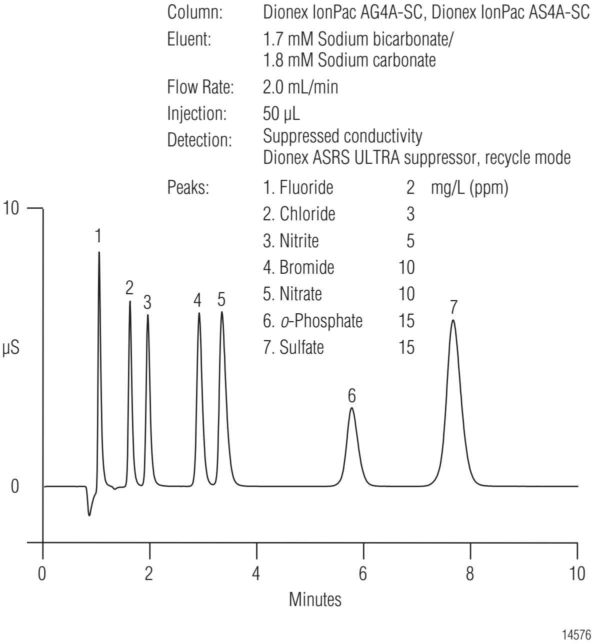
Results and Discussion

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 (ISE) and amperometric titrations.[4] However, many of these methods are not specific and suffer from interferences or limited sensitivity, 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 drinking water and other environmental waters.

Dionex IonPac AS4A-SC Column

U.S. EPA Method 300.0 (A) specifies the use of an Dionex 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 Thermo Scientific™ Dionex™ AMMS™ Anion MicroMembrane suppressor operated in the chemical regeneration mode; however, an Thermo Scientific™ Dionex™ 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 shows a typical chromatogram of a standard containing low-ppm levels of common inorganic anions separated using an Dionex IonPac AS4A-SC column as described in Part A of the "Conditions" section. The Dionex IonPac AS4A-SC column has selectivity similar to that of the Dionex IonPac AS4A column, 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) × (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.


Column: Dionex IonPac AG4A-SC, Dionex IonPac 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
Dionex ASRS ULTRA suppressor, recycle mode

Peaks:		mg/L (ppm)
1. Fluoride	2	
2. Chloride	3	
3. Nitrite	5	
4. Bromide	10	
5. Nitrate	10	
6. *o*-Phosphate	15	
7. Sulfate	15	

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

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 standard, 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 Dionex IonPac AS4A-SC column with a Dionex DX-120 system.

Table 3. Linearity, MDL, retention time, and peak area precision obtained using the Dionex 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)	0.17%	0.17%
***o*-Phosphate**	0.1–100	0.9967	17.8 (5.8 as PO_4-P)	0.35%	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 Dionex IonPac AS4A-SC column for common anions spiked into drinking water, raw (unprocessed) drinking water, and other environmental water matrices. In this instance, the samples were spiked with the analytes at approximately the same levels as specified in U.S. EPA Method 300.0.[3]

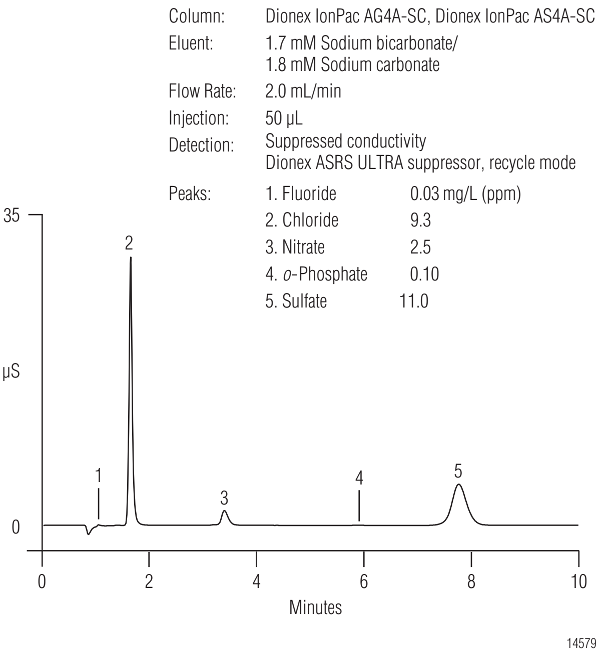
Figure 2 shows a typical chromatogram of inorganic anions in Sunnyvale, California drinking water obtained using the Dionex IonPac AS4A-SC column. Figure 3 shows a chromatogram of inorganic anions in surface water obtained from a lake in Utah. In general, Table 4 shows that acceptable recovery data (i.e., 80–120%) was obtained for the inorganic anions in most matrices. The one exception was the domestic wastewater sample, where fluoride gave a recovery of <60% 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 Dionex IonPac AS4A column.[3] 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 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.

Table 4. Anion recoveries for spiked water samples obtained using the Dionex 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

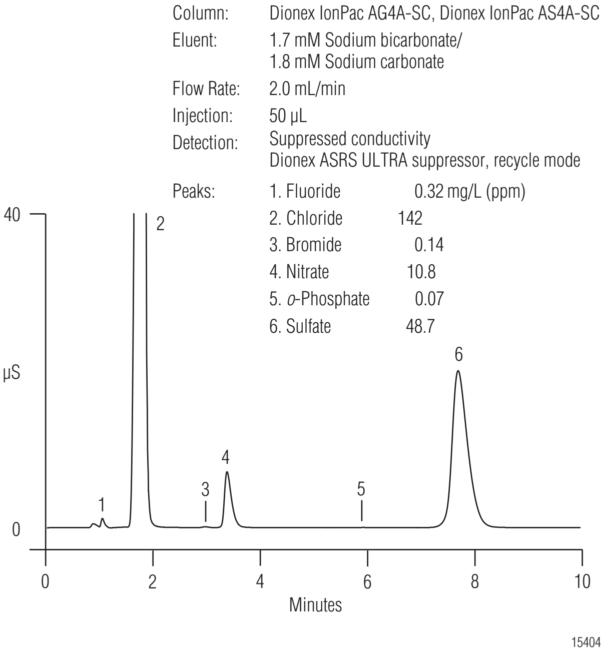
** Sample stored for longer than recommended holding time; inappropriate recovery due to microbial action.*



Column: Dionex IonPac AG4A-SC, Dionex IonPac 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
Dionex ASRS ULTRA suppressor, recycle mode

Peaks:		
1. Fluoride	0.03	mg/L (ppm)
2. Chloride	9.3	
3. Nitrate	2.5	
4. *o*-Phosphate	0.10	
5. Sulfate	11.0	

Figure 2. Determination of inorganic anions in drinking water using a Dionex IonPac AS4A-SC column.



Column: Dionex IonPac AG4A-SC, Dionex IonPac 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
Dionex ASRS ULTRA suppressor, recycle mode

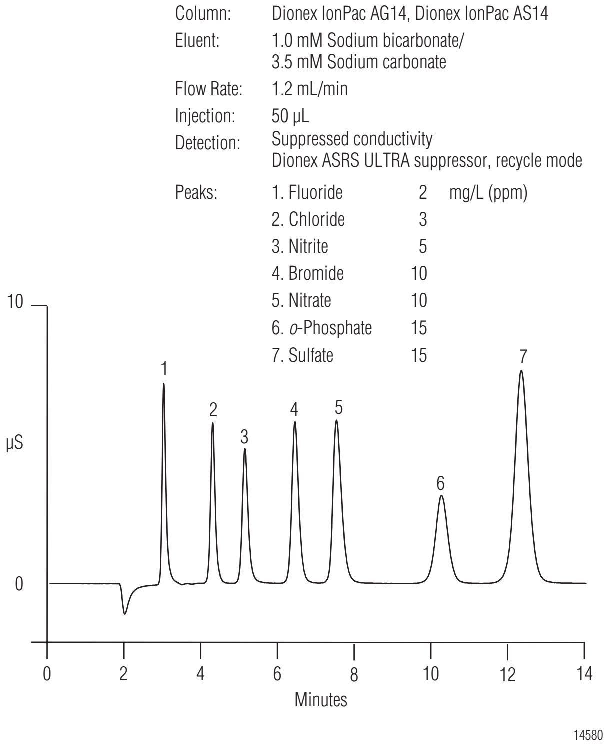
Peaks:
1. Fluoride 0.32 mg/L (ppm)
2. Chloride 142
3. Bromide 0.14
4. Nitrate 10.8
5. *o*-Phosphate 0.07
6. Sulfate 48.7

Figure 3. Determination of anions in surface water using a Dionex IonPac AS4A-SC column.

Dionex IonPac AS14 Column

Although U.S. EPA Method 300.0 specifies the use of an Dionex 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 Dionex IonPac AS14 column is packed with a grafted, methacrylate-based anion-exchange resin. In contrast, the Dionex IonPac AS4A-SC column is packed with a functionalized latex on the surface of an EVB/DVB-based material. The Dionex IonPac AS14 column provides complete resolution of fluoride from formate and/or acetate, in addition to improved resolution of fluoride from the void peak.

The improved selectivity and higher capacity of the Dionex IonPac AS14 column (65 µeq/column compared to 20 µeq/column for the Dionex IonPac AS4A column) also allows improved resolution of chloride and nitrite, which is important in environmental water analysis. One drawback of using the grafted, higher capacity Dionex IonPac AS14 column is lower peak efficiencies than those obtained using the latex-agglomerated Dionex IonPac AS4A-SC column. Figure 4 shows a typical chromatogram of a standard containing low-ppm levels of common anions separated using the Dionex IonPac AS14 column as described in Part B of the "Conditions" section. Fluoride is clearly resolved from the 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.



Column: Dionex IonPac AG14, Dionex IonPac AS14
Eluent: 1.0 mM Sodium bicarbonate/
3.5 mM Sodium carbonate
Flow Rate: 1.2 mL/min
Injection: 50 µL
Detection: Suppressed conductivity
Dionex ASRS ULTRA suppressor, recycle mode

Peaks:
1. Fluoride 2 mg/L (ppm)
2. Chloride 3
3. Nitrite 5
4. Bromide 10
5. Nitrate 10
6. *o*-Phosphate 15
7. Sulfate 15

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

The method linearity using the Dionex IonPac 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 Dionex IonPac AS14 column with a Dionex DX-500 system.

Table 5. Linearity, MDL, retention time, and peak area precision obtained using the Dionex 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*

The performance of the Dionex IonPac 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 Dionex IonPac AS14 column for common anions spiked into drinking water, raw drinking water, and other environmental water matrices.

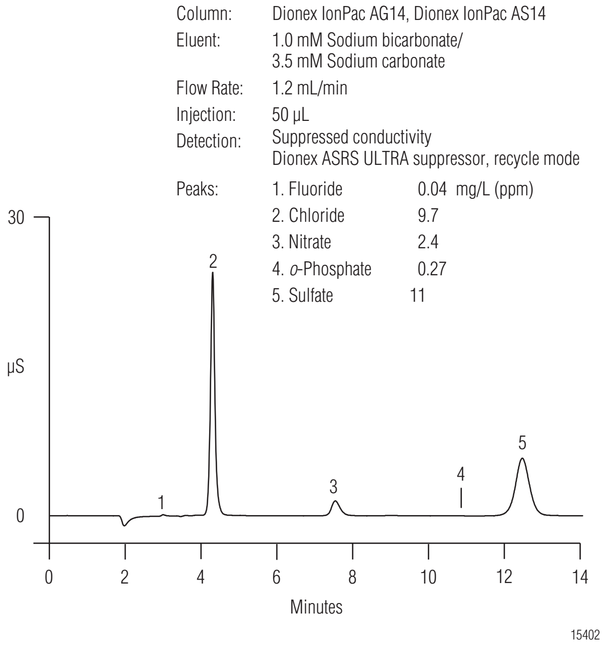
Figure 5 shows a chromatogram of inorganic anions in the same Sunnyvale, California drinking water obtained using the Dionex IonPac AS14 column, and Figure 6 shows a chromatogram of inorganic anions in raw water. Table 6 shows that acceptable recovery data (i.e., 80–120%) was obtained for the inorganic anions in all matrices when using the Dionex AS14 column, with the exception of nitrite and nitrate in the domestic wastewater sample. However, as discussed previously, this was due to the presence of nitrifying/denitrifying microbes rather than any chromatographic resolution problems.

Table 6. Anion recoveries for spiked water samples obtained using the Dionex 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

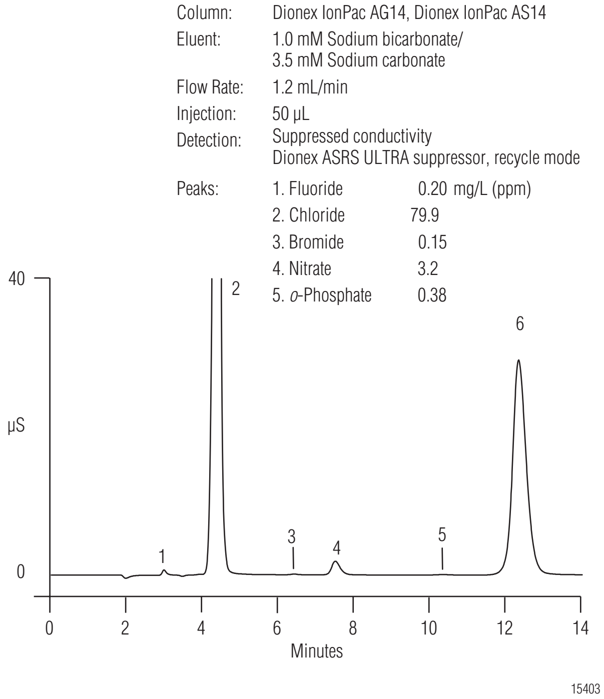
Anion	Domestic Wastewater		Industrial Wastewater		Soil Extract	
	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)	Amt. Added (mg/L)	Recovery (%)
Fluoride	1	90.8	1	90.1	2	101.1
Chloride	20	87.3	20	96.7	5	96.7
Nitrite	2	0.0*	2	98.2	2	89.3
Bromide	2	96.8	2	96.2	2	89.9
Nitrate	5	15.3*	5	95.1	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.*



Column: Dionex IonPac AG14, Dionex IonPac AS14
Eluent: 1.0 mM Sodium bicarbonate/
3.5 mM Sodium carbonate
Flow Rate: 1.2 mL/min
Injection: 50 µL
Detection: Suppressed conductivity
Dionex ASRS ULTRA suppressor, recycle mode
Peaks: 1. Fluoride 0.04 mg/L (ppm)
2. Chloride 9.7
3. Nitrate 2.4
4. *o*-Phosphate 0.27
5. Sulfate 11

Figure 5. Determination of inorganic anions in drinking water using a Dionex IonPac AS14 column.



Column: Dionex IonPac AG14, Dionex IonPac AS14
Eluent: 1.0 mM Sodium bicarbonate/
3.5 mM Sodium carbonate
Flow Rate: 1.2 mL/min
Injection: 50 µL
Detection: Suppressed conductivity
Dionex ASRS ULTRA suppressor, recycle mode
Peaks: 1. Fluoride 0.20 mg/L (ppm)
2. Chloride 79.9
3. Bromide 0.15
4. Nitrate 3.2
5. *o*-Phosphate 0.38

Figure 6. Determination of anions in raw water using a Dionex IonPac AS14 column.

Conclusion

Both the Dionex IonPac AS4A-SC and Dionex IonPac AS14 columns provide suitable performance for the determination of inorganic anions in drinking waters as outlined in U.S. EPA Method 300.0. The Dionex IonPac AS4A-SC column is recommended for the rapid analysis of anions in low-ionic-strength, well-characterized samples such as drinking, raw, and surface water. TheDionex IonPac AS14 column provides improved fluoride resolution from the system void peak and complete resolution of fluoride from formate and/or acetate. The improved selectivity, along with higher capacity, makes the Dionex IonPac AS14 column a better choice for higher-ionicstrength water samples and more complex matrices, such as domestic and industrial wastewaters.

References

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