APPLICATION NOTE 73607

Determination of inorganic anions in drinking water, wastewater, and high ionic strength water

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Goal

To demonstrate the determination of inorganic anions in drinking water, wastewater, and high ionic strength water using an ion chromatography (IC) system with a Thermo Scientific™ Dionex™ IonPac™ AS29-Fast-4µm column

Introduction

Ion chromatography (IC) is a well-accepted technique for monitoring inorganic anions in water, including surface, ground, drinking, and wastewaters. In the U.S., water quality is regulated through the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).[1,2] The SDWA ensures the integrity and safety of U.S. drinking water, and the goal of the CWA is to minimize the discharge of pollutants into the environment. IC methods have been approved for compliance monitoring of inorganic anions in drinking water since the 1980s through U.S. EPA Method 300.0[3] that was updated in 1997 to U.S. EPA Method 300.1[4]. As an approved CWA Test Method, IC was adopted for wastewater analysis under the U.S. EPA Office of Water and the National Pollution Discharge Elimination System (NPDES) permits program.[2-5] In addition, many standard-setting organizations (including the International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM), and American Water Works Association (AWWA)) have validated IC methods for the determination of inorganic anions.[6,7]

IC methods for environmental water analysis have been demonstrated in Thermo Scientific™ Dionex™ Application Notes using standard or microbore flow rate columns with both carbonate/bicarbonate and hydroxide eluents.[8-12] Dionex IonPac AS29-Fast-4µm IC columns are specifically designed to handle high ionic strength samples. These columns easily separate the common inorganic anions in

less than 10 min, can tolerate samples with high or low pH without sample pretreatment, and are ideal for analyzing drinking water, wastewater, process streams, and scrubber solutions.

This application note (AN) demonstrates the determination of inorganic anions in water samples (both drinking water and wastewater) using a Thermo Scientific™ Dionex™ ICS-5000+ Ion Chromatography system with a Dionex IonPac AS29-Fast-4µm anion-exchange column. The AN will also show the benefits of this column compared to a Thermo Scientific™ Dionex™ IonPac™ AS4A-SC column, the column originally specified in U.S. EPA Method 300.0 Part A.

Experimental

Equipment and consumables

- A Dionex ICS-5000+ Ion Chromatography (RFIC™) system* was used in this work, which includes:
  - Thermo Scientific™ Dionex™ ICS-5000+ SP/DP Pump module
  - Thermo Scientific™ Dionex™ ICS-5000+ EG Eluent Generator module with high-pressure degasser
  - Thermo Scientific™ Dionex™ ICS-5000+ DC Detector/ Chromatography module with conductivity detector and dual temperature zones
- Thermo Scientific™ Dionex™ AS-AP Autosampler, with 250 µL syringe, 1.2 mL buffer line assembly and 10.0 µL injection loop
- Thermo Scientific™ Chromeleon™ 7.2 Chromatography Data System

*Equivalent results can be achieved using a Thermo Scientific™ Dionex™ ICS-6000 system.

Consumables

- Thermo Scientific™ Dionex™ EGC 500 K_2CO_3 Potassium Carbonate Eluent Generator Cartridge (EGC) (P/N 088453)
- Thermo Scientific™ Dionex™ EPM 500 Electrolytic pH Modifier (P/N 088471)
- Thermo Scientific™ Dionex™ EGC Carbonate Mixer Kit, 4 mm (P/N 088468)
- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor (4 mm) (P/N 088666)
- Thermo Scientific™ Dionex™ IonPac™ AG29-Fast-4µm Guard Column (4 × 30 mm) (P/N 302834)
- Thermo Scientific™ Dionex™ IonPac™ AS29-Fast-4µm Analytical Column (4 × 150 mm) (P/N 302833)
- Thermo Scientific™ Dionex™ IonPac™ AG4A-SC Guard Column (4 × 50 mm) (P/N 043175)
- Thermo Scientific™ Dionex™ IonPac™ AS4A-SC Analytical Column (4 × 250 mm) (P/N 043174)
- Thermo Scientific™ Nalgene™ Syringe filter (0.2 µm, PES membrane)* (P/N 7252520) *Fisher Scientific P/N 09-740-113
- Thermo Scientific™ Dionex™ AS-AP Autosampler vials. 10 mL polystyrene vials and caps with blue septa, package of 100 (PN/ 074228)

System preparation and setup

Figure 1 shows the flow diagram of the IC system. The IC system is plumbed as a Reagent-Free™ IC (RFIC™) system using eluent generation following the Dionex Eluent Generator Cartridges product manual.[13] Install the suppressor in recycle mode.[14]

Reagent and standards

- Degassed deionized (DI) water, 18 MΩ·cm resistance or better
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anion standards

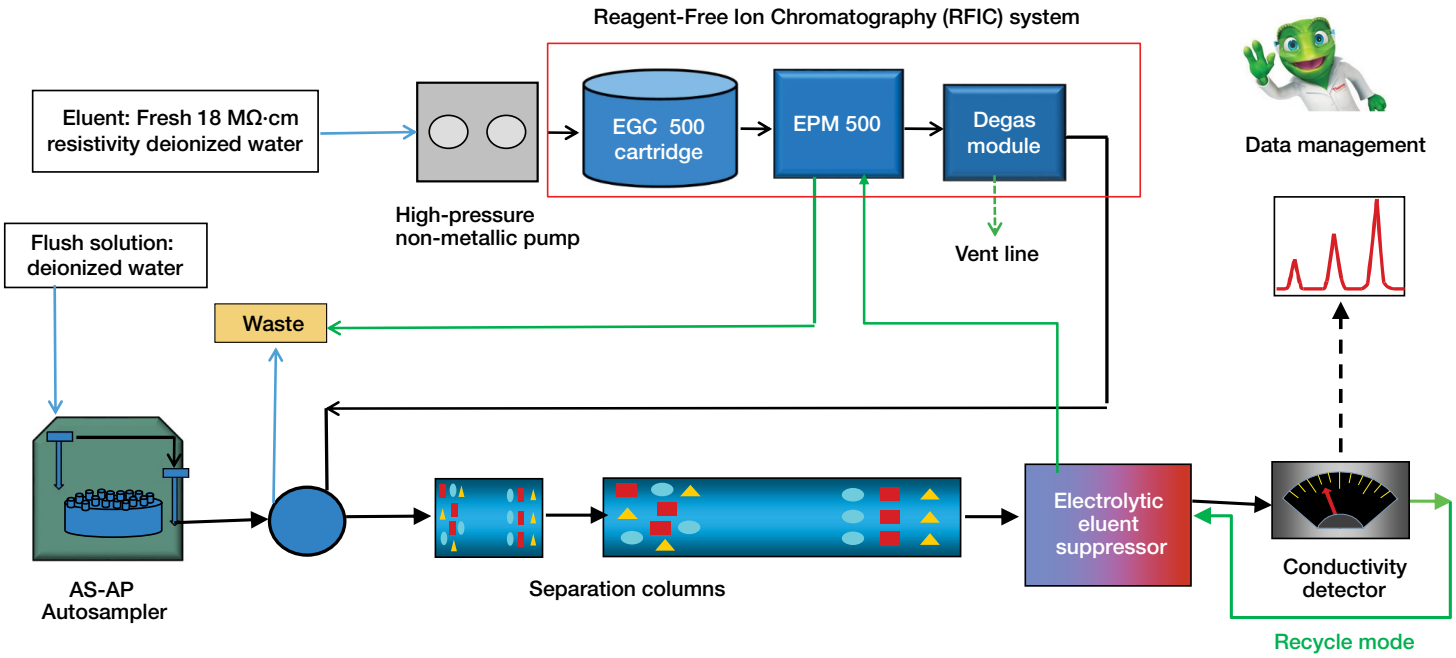


Figure 1. Illustration of the IC system flow diagram

Conditions

Dionex IonPac AS29-Fast-4µm column

Parameter	Setting
Columns	Dionex IonPac AS29-Fast-4µm Analytical column, 4 × 150 mm Dionex IonPac AG29-Fast-4µm Guard column, 4 × 30 mm
Eluent	4.5 mM potassium carbonate, 2.0 mM potassium bicarbonate
Eluent source*	Dionex EGC 500 K_2CO_3 cartridge with an EPM 500 pH modifier and a mixer
Flow rate	1.0 mL/min
Injection volume	10.0 µL (full loop)
Column temperature:	30 °C
Detection	Suppressed conductivity, Dionex ADRS 600 Suppressor, recycle mode, 36 mA current
Detection/suppressor compartment	20 °C
Cell temperature	20 °C
Background conductance	~24.4 µS/cm
System backpressure	~2000 psi (100 psi = 0.689 MPa)
Noise	~2 nS/cm
Run time	10 min

* Manually prepared eluent can be used. If using manual eluents, any Dionex ICS system can be used.

Dionex IonPac AS4A-SC column

Parameter	Setting
Columns	Dionex IonPac AS4A-SC Analytical column, 4 × 250 mm Dionex IonPac AG4A-SC Guard column, 4 × 50 mm
Eluent	1.8 mM potassium carbonate, 1.7 mM potassium bicarbonate
Eluent source*	Dionex EGC 500 K_2CO_3 cartridge with an EPM 500 pH modifier and a mixer
Flow rate	2.0 mL/min
Injection volume	10.0 µL (full loop)
Column temperature	30 °C
Detection	Suppressed conductivity, Dionex ADRS 600 Suppressor, recycle mode, 27 mA current
Detection/suppressor compartment	20 °C
Cell temperature	20 °C
Background conductance	18.2 µS/cm
System backpressure	~1800 psi
Noise	~2 nS/cm
Run time	10 min

* Manually prepared eluent can be used.

Preparation of solutions and reagents

Stock anion standard solutions (1000 mg/L)

Stock standard solutions can be prepared by dissolving the appropriate amounts of the required analytes in 100 mL of DI water according to Table 1. Several of the 1000 mg/L standard solutions are available from Thermo Fisher Scientific, and their part numbers are listed in Table 1. Stock standards for most anions are stable for at least six months at 4 °C. The nitrite and phosphate standards are stable for one month when stored at 4 °C.

Table 1. Masses of compounds used to prepare 100 mL of 1000 mg/L anion standards.

Analyte	1000 mg/L standard P/N	Compound	Amount* (mg)
Fluoride	037158	Sodium fluoride (NaF)	221.0
Chloride	037159	Sodium chloride (NaCl)	164.9
Nitrite-N	Not Available	Sodium nitrite ($NaNO_2$)	492.6
Bromide	Not Available	Sodium bromide (NaBr)	128.8
Nitrate-N	Not Available	Sodium nitrate ($NaNO_3$)	606.8
Phosphate-P	Not Available	Potassium phosphate, monobasic (KH_2PO_4)	439.4
Sulfate	037160	Sodium sulfate (Na_2SO_4)	147.9

*Compound must be dry.

Working standard solutions

Ten levels of calibration standards were used in this study for the determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate (Table 2). All working standard solutions were prepared using the 1000 mg/L stock standards and DI water. The concentrated mixed standards, levels 7, 8, and 9, were prepared and stored at 4 °C (stable for a month). Working standard levels 1 through 6, which contain less than 100 mg/L anions, were prepared fresh daily by diluting the mixed standard level 7 with DI water.

Quality control standard (QCS) and the method detection limits (MDLs) standard

Table 3 shows the anion standard concentrations used to calculate the method detection limits (MDLs) and the composition of the quality control standard (QCS) used to determine retention time and peak area precisions. Because nitrite can convert to nitrate, the mixed standard was prepared on the day of analysis. A more rigorous study to determine MDLs should use single analyte standards.

Table 3. Concentrations of MDL and QCS standards

Analyte	MDL calculation standard (mg/L)	QCS used to test peak retention time and peak area precisions (mg/L)
Fluoride	0.03	2
Chloride	0.02	20
Nitrite-N	0.02	2
Bromide	0.1	2
Nitrate-N	0.02	10
Phosphate-P	0.1	2
Sulfate	0.05	60

Sample preparation

A drinking water sample was collected locally. An environmental wastewater sample was obtained from a local water district lab. Four water samples with high chloride (range: 200 to 100,000 mg/L) at different pH values were provided by a customer.

All samples were filtered through a 0.2 µm PES syringe filter, discarding the first 300 µL of the effluent. To prolong column lifetime, a reversed-phase cartridge can be used to remove hydrophobic organic material from wastewater samples. For the high chloride samples, use a 1 to 100 dilution before analysis when the chloride concentration is >1000 mg/L. Measure the pH of the water samples.

Table 2. Calibration standards (mg/L)

Level	1	2	3	4	5	6	7	8	9	10
Analyte	WSD1	WSD2	WSD3	WSD4	WSD5	WSD6	WSD7	WSD8	WSD9	WSD10
Fluoride	0.1	1	5	10	25	50	100	0	0	0
Chloride	0.2	2	5	20	50	100	200	300	500	1000
Nitrite-N	0.1	1	5	10	25	50	100	0	0	0
Bromide	0.1	1	5	10	25	50	100	0	0	0
Nitrate-N	0.1	1	5	10	25	50	100	0	0	0
Phosphate-P	0.1	1	5	10	25	50	100	0	0	0
Sulfate	0.2	2	5	20	50	100	200	300	500	0

WSD = Working standard

Spiked samples were prepared by adding mixed standards (Spike SD) into the drinking water and wastewater samples.

Table 4. Composition of mixed spiking standards used to spike samples.

Analyte	Spike SD1 (mg/L)	Spike SD2 (mg/L)
Fluoride	100	20
Chloride	200	350
Nitrite-N	100	50
Bromide	100	25
Nitrate-N	100	40
Phosphate-P	100	20
Sulfate	200	350

Results and discussion

Separations

The Dionex IonPac AS29-Fast-4µm column is an anion-exchange column designed for the determination and compliance monitoring of inorganic anions. This column was developed using a unique polymer bonding technology that combines a polymeric 4-µm substrate and a novel hyper-branched anion-exchange condensation polymer to create the stationary phase. This is a high-capacity stationary phase (126 µeq/4 mm column) with optimized selectivity for inorganic anions, and it can tolerate extremely high ionic strength, acidic, or basic samples with minimum loss of performance.[15] This makes the Dionex IonPac AS29-Fast-4µm column an excellent choice for the determination of the common inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate) with minimum sample preparation. It can be used for a variety of sample matrices including drinking water, wastewater, process streams, and scrubber solutions. The column is designed to be used with an isocratic carbonate/bicarbonate eluent, which can be easily prepared from concentrated eluent stock (P/N 302952) or produced by an electrolytic eluent generator.

Figure 2 shows a separation of common anions within 10 min using the Dionex IonPac AS29-Fast-4µm column. As this figure shows, inorganic anions, including seven common anions and carbonate, are well resolved. The peak, or sometimes a dip, caused by carbonate in the sample is located at about 6 minutes and is well separated from nearby nitrate and phosphate peaks for this column (Figure 3). Therefore, this column can be used to analyze samples with high levels of carbonate without affecting the quantification of other analytes.

Columns: Dionex IonPac AG29-Fast-4µm, 4 × 30 mm
Dionex IonPac AS29-Fast-4µm, 4 × 150 mm
Eluent: 4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate: 1.0 mL/min
Inj. volume: 10 µL (full loop)
Column temp.: 30 °C
Detection: Suppressed conductivity,
Dionex ADRS 600 Suppressor (4 mm),
20 °C, 36 mA, recycle mode
Sample: A mixed anions standard

Peaks:		RT (min)	c (mg/L)
1	Fluoride	2.4	10.0
2	Chloride	3.2	20.0
3	Nitrite	3.7	10.0
4	Bromide	4.3	10.0
5	Nitrate	4.7	10.0
6	Carbonate	~6.0	n.a
7	Phosphate	7.0	10.0
8	Sulfate	8.0	20.0

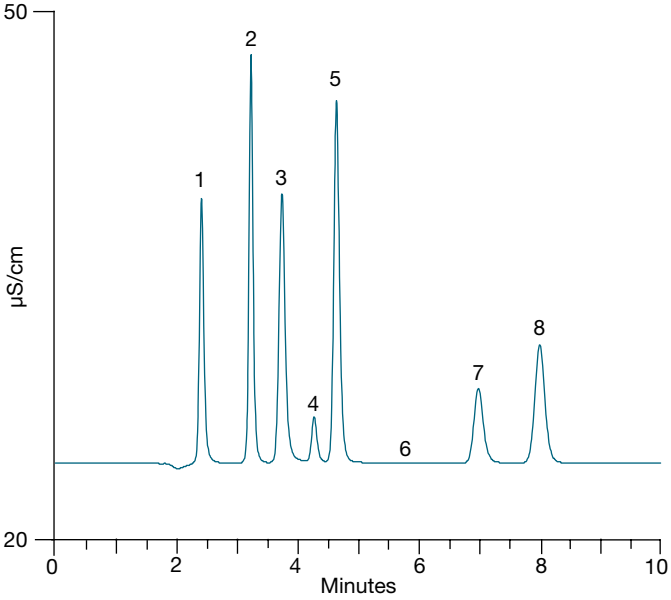


Figure 2. Separation of common anions using the Dionex IonPac AS29-Fast-4µm column

Compared to the Dionex IonPac AS4A-SC column, which is specified in U.S. EPA Method 300.0 Part A, the Dionex IonPac AS29-Fast-4µm column can handle high ionic strength samples and is also able to analyze high and low pH samples without sample pretreatment. Figure 3 compares the separation of the same concentration of common anions standard in a high pH water sample (pH=13) using a Dionex IonPac AS29-Fast-4µm column and a Dionex IonPac AS4A-SC column. As Figure 3 shows:

- For both columns, the total run time to separate common anions is similar (~8 min). The elution order is the same, which allows easy implementation of U.S. EPA Method 300.1 using the Dionex IonPac AS29-Fast-4µm column.

A Columns: Dionex IonPac AG29-Fast-4µm, 4 × 30 mm
Dionex IonPac AS29-Fast-4µm, 4 × 150 mm
Eluent: 4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate: 1.0 mL/min
Inj. volume: 10 µL (full loop)
Detection: Suppressed conductivity,
Dionex ADRS 600 Suppressor (4 mm),
20 °C, 36 mA, recycle mode

B Columns: Dionex IonPac AG4A-SC, 4 x 50 mm
Dionex IonPac AS4A-SC, 4 x 250 mm
Eluent: 1.8 mM Na_2CO_3 /1.7 mM $NaHCO_3$
Flow rate: 2.0 mL/min
Inj. volume: 10 µL (full loop)
Detection: Suppressed conductivity,
Dionex ADRS 600 Suppressor (4 mm),
20 °C, 27 mA, recycle mode

Sample: A mixed anions standard in 0.1 N NaOH

Peaks:	A RT (min)	B RT (min)	c (mg/L)
1 Fluoride	2.4	1.1	5.0
2 Chloride	3.2	1.7	10.0
3 Nitrite	3.7	2.0	5.0
4 Bromide	4.3	3.0	5.0
5 Nitrate	4.7	3.4	5.0
6 Carbonate	~6.0	~1.5	n.a
7 Phosphate	7.0	6.0	5.0
8 Sulfate	8.0	8.2	10.0

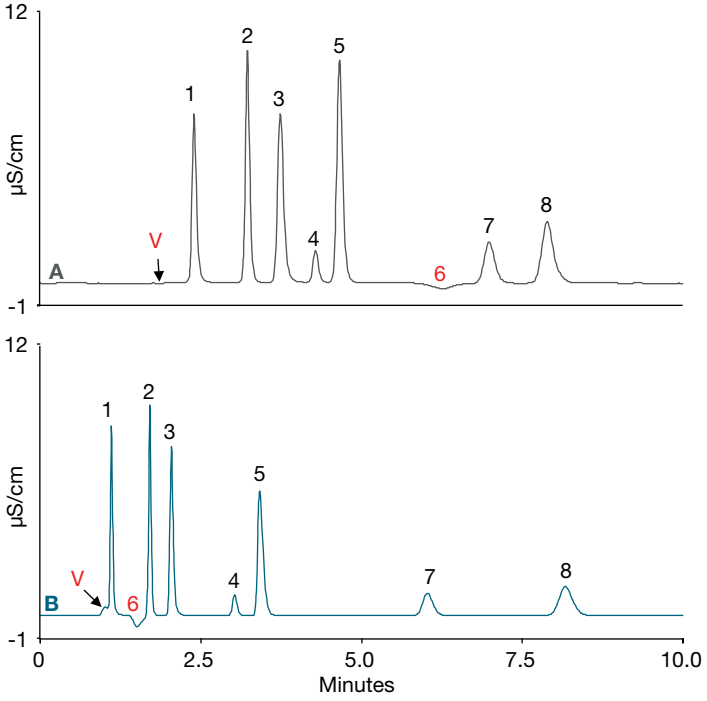


Figure 3. Separation of common anions in a pH 13 water sample using the Dionex IonPac AS29-Fast-4µm column and the Dionex IonPac AS4A-SC column. V indicates the void volume.

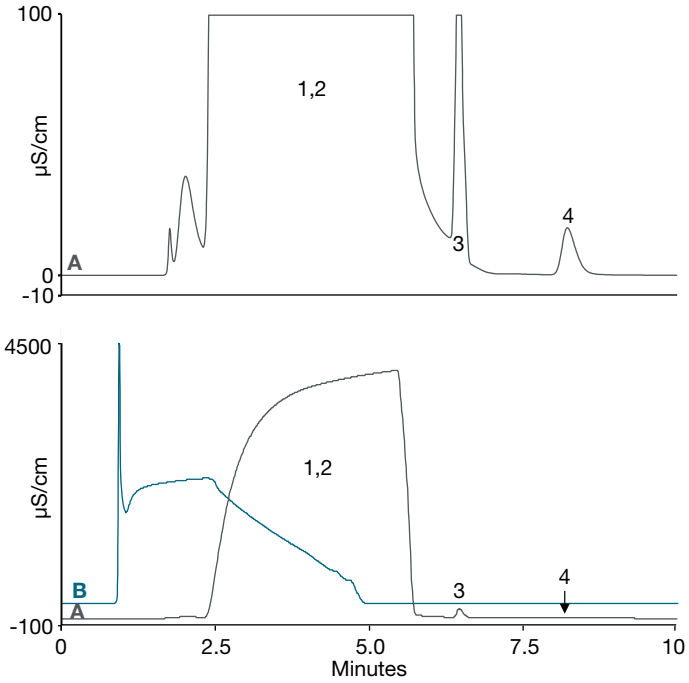
- When the Dionex IonPac AS4A-SC column is used (Figure 3, Panel B), the void volume interferes with the fluoride peak, and the carbonate peak elutes just prior to chloride and can interfere with the integration of the chloride peak. When the Dionex IonPac AS29-Fast-4µm column is used (Figure 3, Panel A), the void volume and carbonate peak are well resolved from the analyte peaks, allowing more accurate determinations of inorganic anions.
- To achieve a similar run time for the common anions, the flow rate was 1.0 mL/min for the Dionex IonPac AS29-Fast-4µm column and 2.0 mL/min for the Dionex IonPac AS4A-SC column. This represents a 50% eluent savings with the Dionex IonPac AS29-Fast-4µm column. These chromatograms show that the Dionex IonPac AS29-Fast-4µm column can replace, and has advantages over, the Dionex IonPac AS4A-SC column for U.S. EPA Method 300.1.

Figure 4 compares chromatograms of a water sample with high chloride concentration using a Dionex IonPac AS29-Fast-4µm column and a Dionex IonPac AS4A-SC column. This figure shows that the Dionex IonPac AS4A-SC column was overloaded and cannot be used for the analysis without sample dilution. However, the Dionex IonPac AS29-Fast-4µm column's high capacity allows this sample to be analyzed without dilution. This sample will be discussed in more detail in the application section.

Linearity, method detection limits, and precision

The quality control section of U.S. EPA Method 300.1 (Section 9.0) requires a demonstration of linearity, MDLs, and acceptable instrument performance by the analysis of a QCS before performing analyses using the method. Here, seven-point calibrations were used for fluoride, nitrite, bromide, nitrate, and phosphate; a ten-point calibration was used for chloride and a nine-point calibration was used for sulfate (Table 2). MDLs were determined by performing seven replicate injections of standards at a concentration of three to five times the estimated instrument detection limits (Table 4). Retention time and peak area precisions were determined from replicate injections of a QCS prepared in DI water (Table 3). Table 5 shows the linear concentration ranges, the coefficients of determination (r^2), calculated MDLs, and retention time and peak area precisions. The method is sensitive for the determination of the seven inorganic anions in environmental waters with low MDLs (0.003 to 0.035 mg/L). Because nitrite can convert to nitrate, changing the concentration of each, the resulting MDLs for nitrate and nitrite should be consider estimates. However, we suspect they are good estimates as the mixed standard was prepared on the day of analysis. The retention time stability is excellent (<0.01%). The peak area precisions are 0.5 to 0.7%, except phosphate precision which is 3.7%, likely due to the low concentration of phosphate in the QCS.

Figure 5 shows the calibration plots. Fluoride, chloride, nitrite, nitrate, and sulfate exhibited a large linear calibration range, but bromide and phosphate did not exhibit a linear response at high concentrations.



A Columns: Dionex IonPac AG29-Fast-4µm, 4 × 30 mm
Dionex IonPac AS29-Fast-4µm, 4 × 150 mm
Eluent: 4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate: 1.0 mL/min
Inj. volume: 10 µL (full loop)
Detection: Suppressed conductivity, Dionex ADRS 600 Suppressor (4 mm), 20 °C, 36 mA, recycle mode

B Columns: Dionex IonPac AG4A-SC, 4 x 50 mm
Dionex IonPac AS4A-SC, 4 x 250 mm
Eluent: 1.8 mM Na_2CO_3 /1.7 mM $NaHCO_3$
Flow rate: 2.0 mL/min
Inj. volume: 10 µL (full loop)
Detection: Suppressed conductivity, Dionex ADRS 600 Suppressor (4 mm), 20 °C, 27 mA, recycle mode

Top panel: Enlargement of the Dionex IonPac AS29-Fast-4µm trace from the lower panel
Lower panel: Full scale
Sample: A high chloride water sample (sample 2)

Peaks:		mg/L
1	Chloride*	86200
2	Bromide*	602
3	Carbonate	n.a
4	Sulfate	60.8

* Note: Determined by testing 100-fold diluted sample

Figure 4. Chromatograms of a water sample with a high chloride concentration using a Dionex IonPac AS29-Fast-4µm column and a Dionex IonPac AS4A-SC column

Table 5. Linearity, method detection limits (MDLs), and retention time and peak area precisions obtained using a Dionex IonPac AS29-Fast-4µm column with a 10 µL injection

Analyte	Range (mg/L)	Coefficient of determination (r^2)	Calculated* MDL (mg/L)	Retention time precision (RSD)	Peak area precision (RSD)
Fluoride	0.01–100	1	0.02	0.1	0.7
Chloride	0.02–1000	0.999	0.004	<0.01	0.5
Nitrite-N	0.01–100	1	0.003	<0.01	0.7
Bromide	0.01–100	0.989 (0.994) **	0.02	<0.01	0.7
Nitrate-N	0.01–100	0.996	0.003	<0.01	0.5
Phosphate-P	0.01–100	0.995 (1.00) **	0.035	<0.01	3.7
Sulfate	0.02–500	0.998	0.01	<0.01	0.6

*MDL = (t) × (S). 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), S = standard deviation of the replicate analyses.

**Calibration type is linear and forced through the origin. The values in parentheses (bromide and phosphate) are quadratic fits that were forced through the origin.

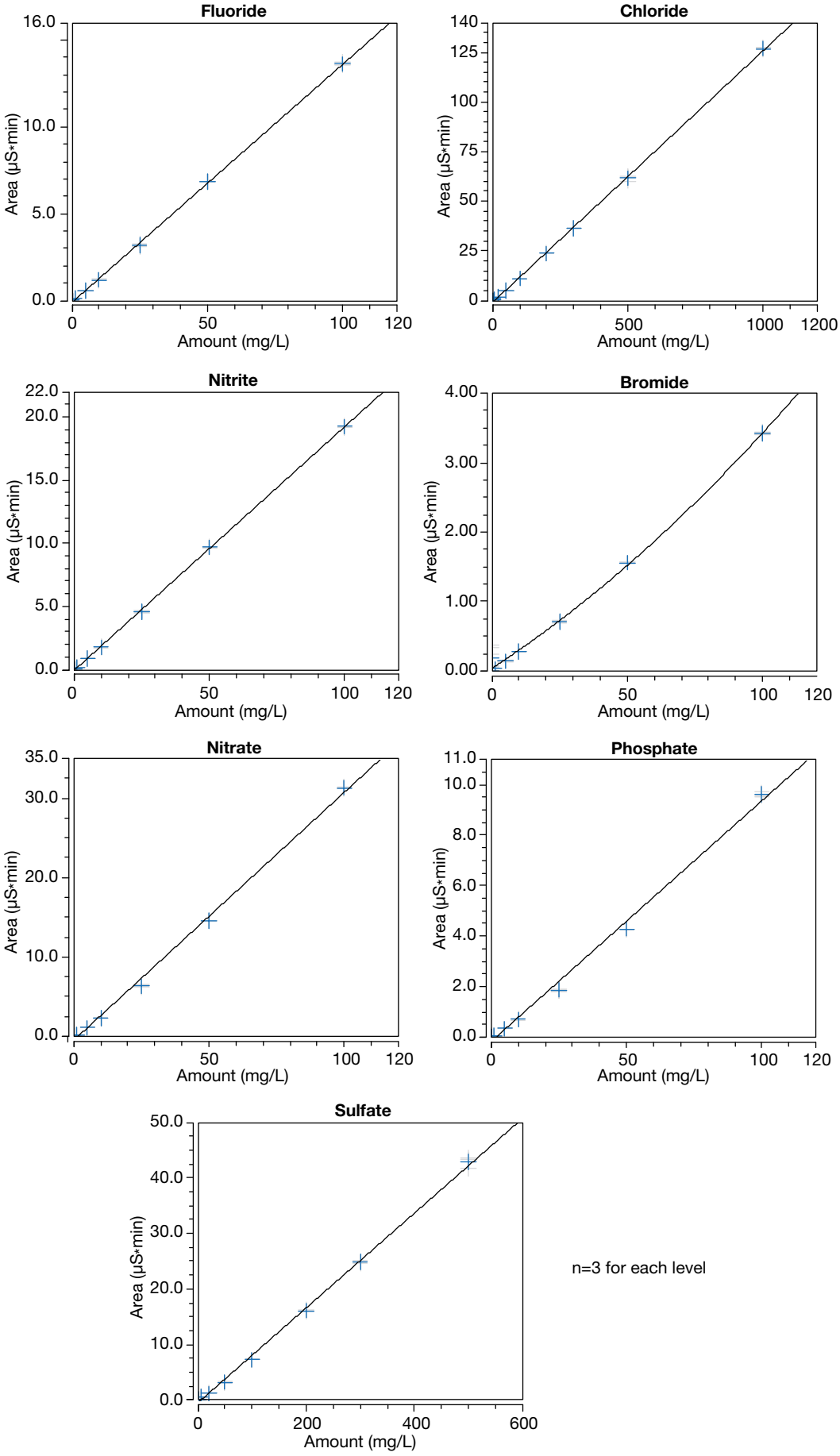


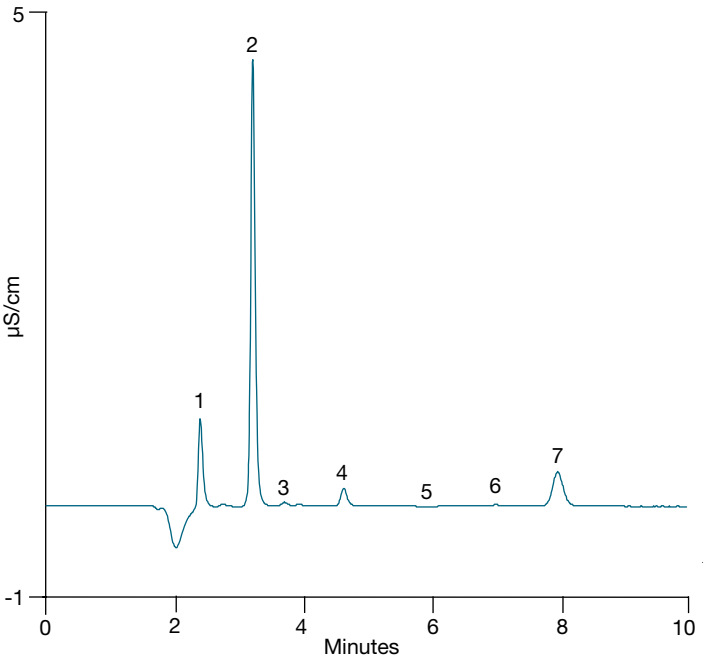
Figure 5. Calibration plots

Example applications of the Dionex IonPac AS29-Fast-4µm column

Using a Dionex IonPac AS29-Fast-4µm column with a 10 µL injection volume, we determined inorganic anions in several types of water samples to demonstrate its applications and advantages.

Inorganic anions in drinking water

The Dionex IonPac AS29-Fast-4µm column can be used for compliance monitoring of inorganic anions in drinking water. Figure 6 shows a chromatogram of a drinking water sample. All anion peaks were well separated in less than 10 min. Table 6 lists the inorganic anions found and the spike recovery results. The results show that the drinking water sample contains chloride (3.13 mg/L) and sulfate (0.8 mg/L) with little fluoride (0.6 mg/L), nitrite (0.03 mg/L), nitrate (0.07 mg/L), and phosphate (0.1 mg/L). The method is precise (RSD range 0.2–1.8%) and accurate (recovery range 90–110%).



Columns:	Dionex IonPac AG29-Fast-4µm, 4 × 30 mm Dionex IonPac AS29-Fast-4µm, 4 ×1 50 mm
Eluent:	4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate:	1.0 mL/min
Inj. volume:	10 µL (full loop)
Column temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ADRS 600 Suppressor (4 mm), 20 °C, 36 mA, recycle mode
Sample:	Drinking water

Peaks:		RT (min)	c (mg/L)
1	Fluoride	2.4	0.60
2	Chloride	3.2	3.13
3	Nitrite	3.7	0.03
4	Nitrate	4.7	0.07
5	Carbonate	~6.0	n.a
6	Phosphate	7.0	0.10
7	Sulfate	8.0	0.80

Figure 6. Determination of inorganic anions in drinking water using a Dionex IonPac AS29-Fast-4µm column

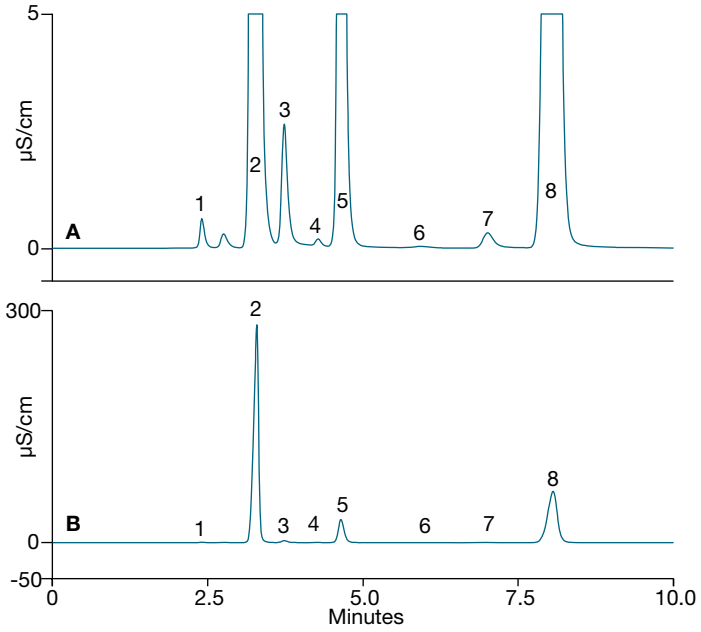
Table 6. Determination of common inorganic anions in a drinking water sample and the spike recovery results

		Water sample		Spike recovery			
Analyte	RT (min)	Anion conc.* (mg/L)	RSD	Added (mg/L)	Recovery (%)	Added (mg/L)	Recovery (%)
Fluoride	2.4	0.60 ± 0.01	1.15	0.4	101	2.0	90
Chloride	3.2	3.13 ± 0.01	0.21	6.2	96	35.0	101
Nitrite-N	3.7	0.03 ± 0.00	2.8	0.9	91	5.0	93
Bromide	4.3	0	n. a	0.4	92	2.5	94
Nitrate-N	4.7	0.07 ± 0.00	1.3	0.7	94	4.0	90
Phosphate-P	7.0	0.1 ± n.a	n. a	0.4	110	2.0	100
Sulfate	8.0	0.8 ± 0.01	1.8	6.2	98	35.0	98

* The samples were tested twice on separate days, triplicate injections per day

Inorganic anions in wastewater

The Dionex IonPac AS29-Fast-4µm column can also be used for compliance monitoring of inorganic anions in wastewater. Figure 7 shows a chromatogram of inorganic anions in a wastewater sample. Table 7 lists the inorganic anions found in the wastewater and the spike recovery results. Compared to drinking water, the wastewater sample contains high levels of chloride (222.5 mg/L), nitrate (10.99 mg/L), and sulfate (152.8 mg/L) with little fluoride (0.37 mg/L), nitrite (1.75 mg/L), and phosphate (0.87 mg/L). Again, the method is precise (RSD range 0.4–5.7%) and accurate (recovery range 90–109%).



Columns:	Dionex IonPac AG29-Fast-4µm, 4 × 30 mm Dionex IonPac AS29-Fast-4µm, 4 × 150 mm
Eluent:	4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate:	1.0 mL/min
Inj. volume:	10 µL (full loop)
Column temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ADRS 600 Suppressor (4 mm), 20 °C, 36 mA, recycle mode
Top panel:	Zoomed in
Lower panel:	Full scale
Sample:	Wastewater

Peaks:		RT (min)	c (mg/L)
1	Fluoride	2.4	0.37
2	Chloride	3.3	223
3	Nitrite	3.7	1.75
4	Bromide	4.3	0.91
5	Nitrate	4.6	11.0
6	Carbonate	~6.0	n.a
7	Phosphate	7.0	0.87
8	Sulfate	8.1	153

Figure 7. Determination of inorganic anions in wastewater using a Dionex IonPac AS29-Fast-4µm column

Table 7. Common inorganic anions in a wastewater sample and the spike recovery results

		Water sample		Spike recovery			
Analyte	RT (min)	Anion conc.* (mg/L)	RSD	Added (mg/L)	Recovery (%)	Added (mg/L)	Recovery (%)
Fluoride	2.4	0.37 ± 0.02	5.7	3.20	93	10.0	95
Chloride	3.3	222.5 ± 0.9	0.4	56.0	97	20.0	93
Nitrite-N	3.7	1.75 ± 0.02	1.2	8.00	103	10.0	102
Bromide	4.3	0.91 ± 0.01	1.1	4.00	91	10.0	107
Nitrate-N	4.6	10.99 ± 0.05	0.4	6.40	103	10.0	94
Phosphate-P	7.0	0.87 ± 0.05	5.6	3.20	90	10.0	95
Sulfate	8.1	152.8 ± 0.6	0.4	56.0	109	20.0	92

* The samples were tested twice on separate days, triplicate injections per day

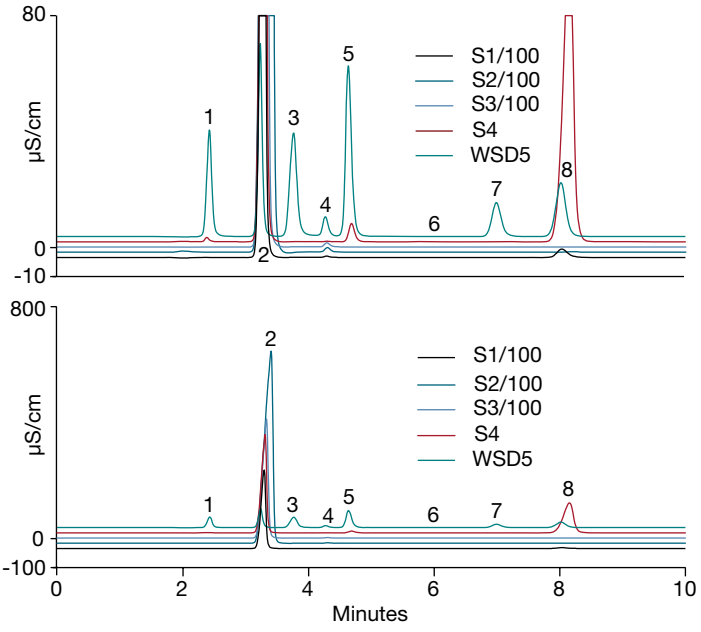
Inorganic anions in challenging water samples

Four water samples with high chloride concentrations (200 to 100,000 mg/L) and different pH values were studied. The inorganic anions were determined using a Dionex IonPac AS29-Fast-4µm column with a 10 µL injection. Because the chloride concentrations of three samples were above the highest calibration level (1000 mg/L), dilution was required. The results are shown below (Table 8 and Figure 8). Because the Dionex IonPac AS29-Fast-4µm column features a robust stationary phase designed to tolerate acidic (e.g., sample in sulfuric acid matrix) and basic samples,[15] the high ionic strength samples that are either acidic or basic (pH range 2 to 9 for the original samples) can be analyzed with the Dionex IonPac AS29-Fast-4µm column without compromising the separation. These samples were analyzed directly or with minimum sample preparation (filtration and one dilution) regardless of their pH.

Table 8. Inorganic anions found in the water samples with high chloride concentrations at different pH values

	Sample 1 (S1)*		Sample 2 (S2)*		Sample 3 (S3)*		Sample 4 (S4)	
	Anions (mg/L)	RSD	Anions (mg/L)	RSD	Anions (mg/L)	RSD	Anions (mg/L)	RSD
Sample pH	6.5		2.0		6.0		9.0	
Fluoride	5	20	0	-	0	-	0.87	1.1
Chloride	20,500	0.6	86,200	0.4	38,200	0.21	282	1.1
Nitrite-N	0	-	0	-	0	-	0	-
Bromide	175	1.1	602	0.5	560	1.5	0.54	1.4
Nitrate-N	0	-	0	-	0	-	2.32	1.0
Phosphate-P	28	10	0	-	0	-	0.24	10
Sulfate	738	0.8	60.9	2.5	19	5.7	243	1.1

*Water samples 1 to 3 were analyzed after a 100-fold dilution. Water sample 4 was measured without dilution. All samples were injected three times



Columns: Dionex IonPac AG29-Fast-4µm, 4 × 30 mm
Dionex IonPac AS29-Fast-4µm, 4 × 150 mm
Eluent: 4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate: 1.0 mL/min
Inj. volume: 10 µL (full loop)
Column temp.: 30 °C
Detection: Suppressed conductivity,
Dionex ADRS 600 Suppressor (4 mm),
20 °C, 36 mA, recycle mode

Sample		S1/100*	S2/100*	S3/100*	S4	WSD5	
Peaks		(mg/L)	(mg/L)	(mg/L)	(mg/L)	RT (min)	(mg/L)
1	Fluoride	0.047	0	0	0.87	2.4	25
2	Chloride	205	862	382	282	3.2	50
3	Nitrite-N	0	0	0	0	3.7	25
4	Bromide	1.75	6.02	5.60	0.54	4.3	25
5	Nitrate-N	0	0	0	2.32	4.7	25
6	Carbonate	n.a.	n.a.	n.a.	n.a.	~ 6	n.a.
7	Phosphate-P	27.9	0	0	0.24	7.0	25
8	Sulfate	738	0.609	0.190	243	8.0	50

*Diluted 1 to 100

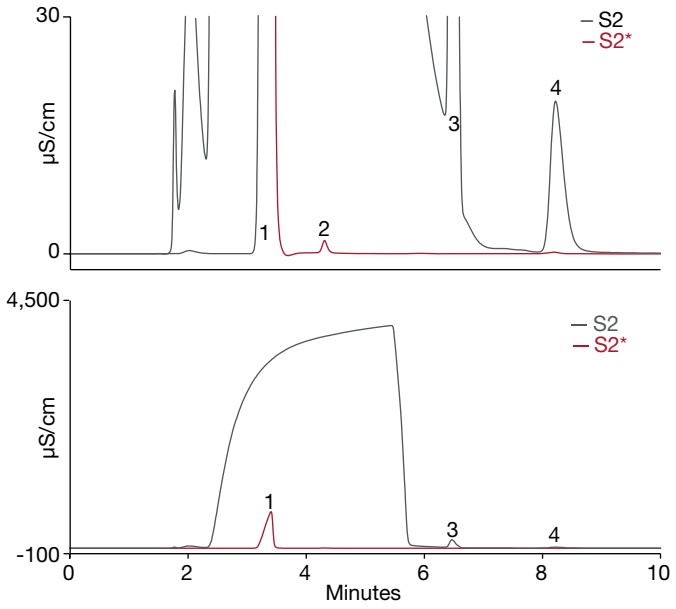
Figure 8. Determination of inorganic anions in high ionic strength water samples using a Dionex IonPac AG29-Fast-4µm column

Sulfate in a high salt matrix

The unique chemistry of the Dionex IonPac AS29-Fast-4µm column has been designed to handle high ionic strength samples without compromising analyte separation. The high capacity and unique selectivity make the Dionex IonPac AS29-Fast-4µm column an ideal column for the determination of a sample's sulfate content. The results of the high chloride concentration water sample 2 (S2) with and without dilution are shown in Table 9 and Figure 9. The sulfate result is almost the same (60.8 vs. 60.9 mg/L) even at such high concentration of chloride (86,200 mg/L). The method is robust to determine sulfate in various water samples.

Table 9. Determination of sulfate content in a high chloride concentration water sample using a Dionex IonPac AS29-Fast-4µm column with and without dilution

Sample preparation	Chloride (mg/L)	Bromide (mg/L)	Sulfate
None	Not determined	Not determined	60.8 ± 0.8
1 to 100 sample dilution	86200	602	60.9 ± 1.5



Columns: Dionex IonPac AG29-Fast-4µm, 4 × 30 mm
Dionex IonPac AS29-Fast-4µm, 4 × 150 mm
Eluent: 4.5 mM Na_2CO_3 /2.0 mM $NaHCO_3$
Flow rate: 1.0 mL/min
Inj. volume: 10 µL (full loop)
Column temp.: 30 °C
Detection: Suppressed conductivity, Dionex ADRS 600 Suppressor (4 mm), 20 °C, 36 mA, recycle mode
Top panel: Zoomed in
Lower panel: Full scale
Samples: Gray: S2, high chloride water sample S2
Red: S2*, 100-fold diluted S2

Peaks:	S2 (mg/L)	S2* (mg/L)
1 Chloride	ND	862
2 Bromide	ND	6.02
3 Unknown	n.a	n.a
4 Sulfate	60.8	0.609

*Diluted 1 to 100

Figure 9. Chromatograms of the determination of sulfate in a high chloride water sample using a Dionex IonPac AS29-Fast-4µm column with and without sample dilution

Conclusion

This Application Note describes a method for the determination of inorganic anions in water using a Dionex IonPac AS29-Fast-4µm column. The study demonstrated that the method has a large linear range (e.g., 0.02 to 1000 mg/L for chloride), is sensitive, precise, and accurate. The method was shown to be robust and was used for several types of water samples (drinking water, wastewater, and water with high ionic strength (chloride ranged from 282 to 86,200 mg/L)) and different pH values (2 to 9). Compared to the Dionex IonPac AS4A-SC column, the Dionex IonPac AS29-Fast-4µm column has improved selectivity and higher capacity, making it a better choice for compliance monitoring of inorganic anions, especially for high-ionic strength water and other challenging samples.

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