

Determination of Inorganic Anions in Wastewater by Ion Chromatography

Peter Jackson
Thermo Fisher Scientific Inc.

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 safety of U.S. drinking water, and the goal of the CWA is to reduce the discharge of pollutants into U.S. waters.^{1,2} IC 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 determination 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 Thermo Scientific™ Dionex™ IonPac™ AS14 column and Dionex IonPac AS9-HC 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 system is a dedicated ion chromatograph; the Dionex DX-500 system 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 AD20 UV-Vis 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 Workstation were used with both systems. Equivalent or improved results can be achieved using a Thermo Scientific Dionex ICS-1100 or a Thermo Scientific Dionex ICS-1600 system.*

Reagents and Standards

- Deionized water, Type I reagent grade, 18 M Ω -cm resistance or better
- 0.18 M Sodium carbonate/0.17 M Sodium bicarbonate
- 0.35 M Sodium carbonate/0.1 M Sodium bicarbonate
- 0.5 M Sodium carbonate
- 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
- Nitrite 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 μ L |
| 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 μ S |

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 μ L |
| Detection: | Suppressed conductivity, Dionex ASRS ULTRA suppressor (4 mm), recycle mode, 100 mA current |
| System Backpressure: | ~1600 psi |
| Background Conductance: | ~17 μ S |

Part C

| | |
|-------------------------|--|
| Columns: | Dionex IonPac AG9-HC, 4 × 50 mm Dionex IonPac AS9-HC, 4 × 250 mm |
| Eluent: | 9.0 mM Sodium carbonate |
| Run Time: | <24 min |
| Flow Rate: | 1.0 mL/min |
| Injection Volume: | 50 μ L |
| Detection: | Suppressed conductivity, Dionex ASRS ULTRA suppressor (4 mm), recycle mode, 100 mA current |
| System Backpressure: | ~2200 psi |
| Background Conductance: | ~22 μ S |

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 ₂ PO ₄) | 1.433 |
| Sulfate | Sodium sulfate (Na ₂ SO ₄) | 1.522 |

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 |
| <i>o</i> -Phosphate | 0.1–100 | 0.045 | 2 |
| Sulfate | 0.2–200 | 0.050 | 60 |

Eluent Solutions

For the Dionex IonPac AS4A-SC and Dionex IonPac AS14 columns, dilute 20 mL of the appropriate eluent concentrate to 2.0 L with deionized water. For the Dionex 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 U.S. EPA Method 300.0.³ The domestic wastewater sample was treated with a C₁₈ Sep-Pak cartridge to remove hydrophobic organic material in order to prolong column lifetimes.⁶ The C₁₈ 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.

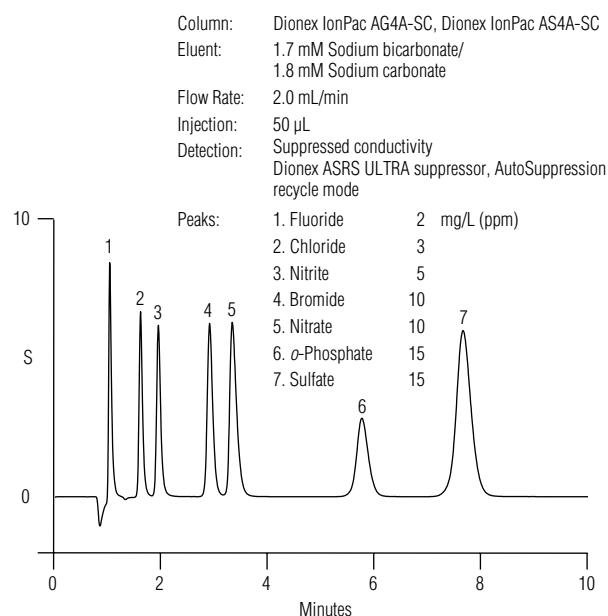
Results and Discussion

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.

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 a Thermo Scientific™ Dionex™ AMMS™ Anion MicroMembrane suppressor operated in the chemical regeneration mode; however, a 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 pellicular Dionex IonPac AS4A-SC column has an outer layer of latex with selectivity similar to that of the Dionex IonPac AS4A column, although the substrate of the Dionex IonPac AS4A-SC column is ethylvinylbenzene (EVB)



14576

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

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 $(t) \times (SD)$ 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 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 ($\mu\text{g/L}$) | 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 $\text{NO}_2\text{-N}$) | <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 $\text{NO}_3\text{-N}$) | 0.17% | 0.17% |
| <i>o</i> -Phosphate | 0.1–100 | 0.9967 | 17.8 (5.8 as $\text{PO}_4\text{-P}$) | 0.35% | 0.35% |
| Sulfate | 0.2–200 | 0.9975 | 6.7 | <0.05% | 0.14% |

^a Dionex DX-120 system

^b $\text{MDL} = \sigma \cdot t_{\alpha, n-1}$ where $t_{\alpha, n-1} = 3.14$ for $n = 7$

^c $\text{RSD} = \text{Relative standard deviation}, n = 7$

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 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

Figure 2A shows a chromatogram of inorganic anions in industrial wastewater from a chemical manufacturing plant obtained using the Dionex 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.

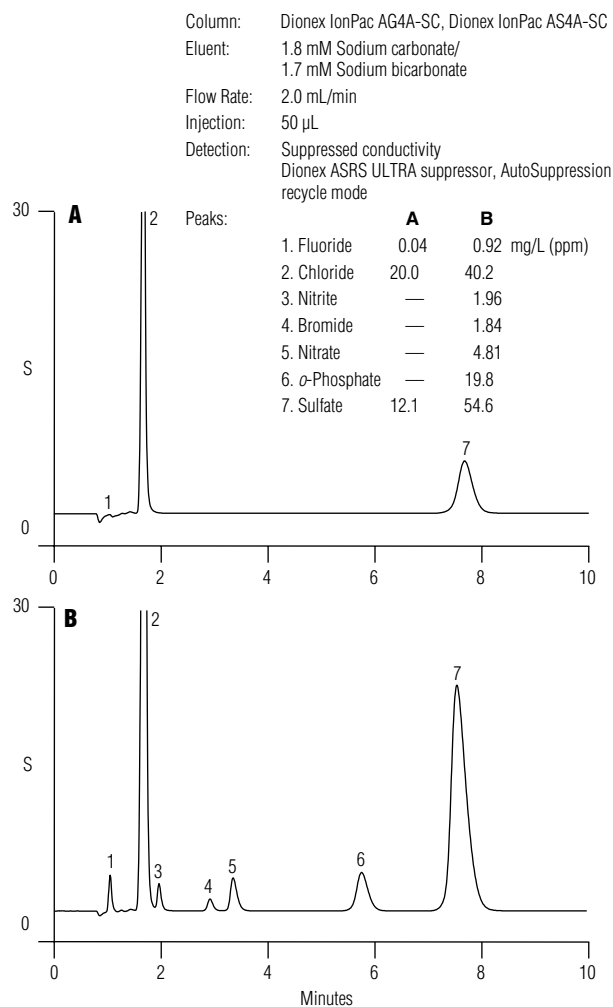


Figure 2. Determination of inorganic anions in A) industrial wastewater and B) spiked industrial wastewater using a Dionex IonPac AS4A-SC column.

Table 4. Anion recoveries for spiked water samples obtained using the Dionex IonPac AS4A-SC column.

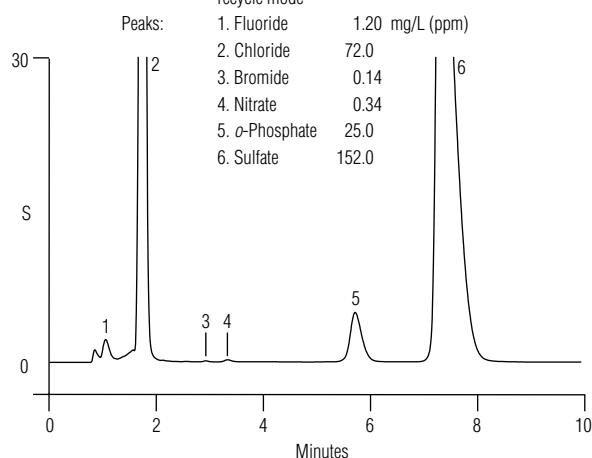
| Anion | Drinking Water | | Raw Water | | Surface Water | |
|---------------------|---------------------|--------------|-----------------------|--------------|-------------------|--------------|
| | Amt. Added (mg/L) | Recovery (%) | Amt. Added (mg/L) | Recovery (%) | Amt. Added (mg/L) | Recovery (%) |
| 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 |
| <i>o</i> -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 |
| <i>o</i> -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.

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 Dionex IonPac 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 than 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: 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, AutoSuppression
 recycle mode



15769

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

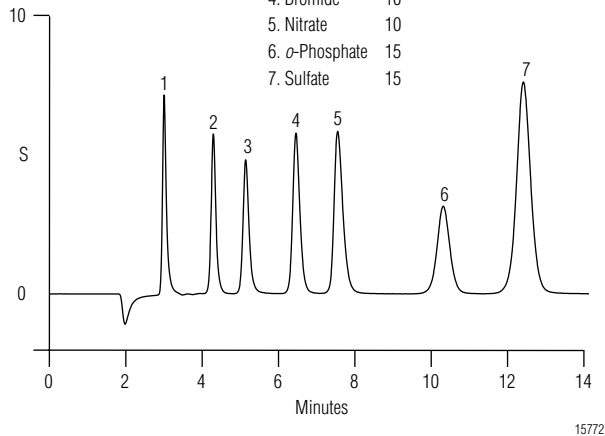
Dionex IonPac AS14 Column

While U.S. EPA Method 300.0 specifies the use of a 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 methacrylate-based functional group grafted onto the surface of a macroporous resin consisting of EVB crosslinked with 55% DVB. The Dionex IonPac 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 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 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.

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



15772

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

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 (μ g/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% |
| <i>o</i> -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 = $\sigma \cdot t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$

^c RSD = Relative standard deviation, $n = 7$

data that can be obtained for inorganic anions using the Dionex IonPac AS14 column with a Dionex DX-500 system. The performance of the Dionex IonPac AS14 column 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 industrial wastewater, domestic wastewater, and other environmental water matrices.

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 |
| <i>o</i> -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 |
| <i>o</i> -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 Dionex 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 Dionex IonPac 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 Dionex IonPac AS4A-SC column.

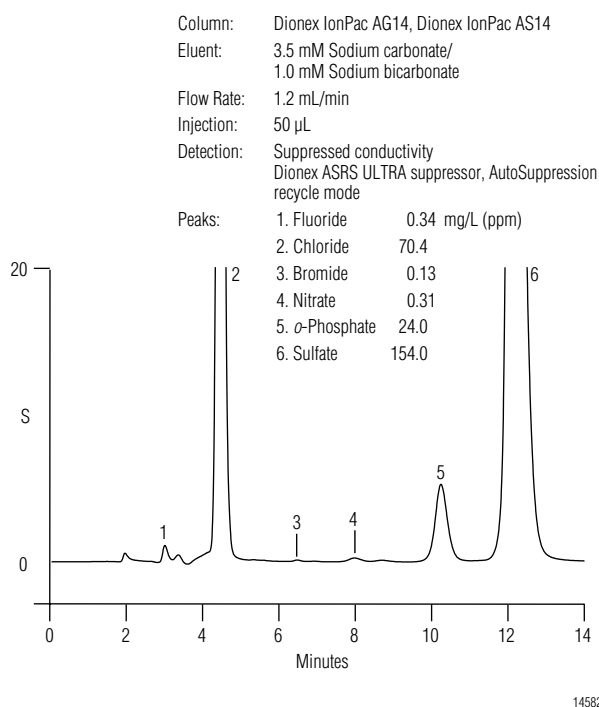


Figure 5. Determination of inorganic anions in domestic wastewater using a Dionex IonPac AS14 column.

Dionex IonPac AS9-HC Column

The Dionex 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 Dionex IonPac 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 μ eq/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 Dionex 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 Dionex IonPac AS4A-SC and Dionex IonPac AS14 columns, hence the Dionex IonPac AS9-HC column is ideal for the analysis of samples containing dissimilar levels of inorganic anions. The disadvantages of using the high capacity Dionex IonPac 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 Dionex IonPac AS4A-SC and Dionex IonPac AS14 columns.

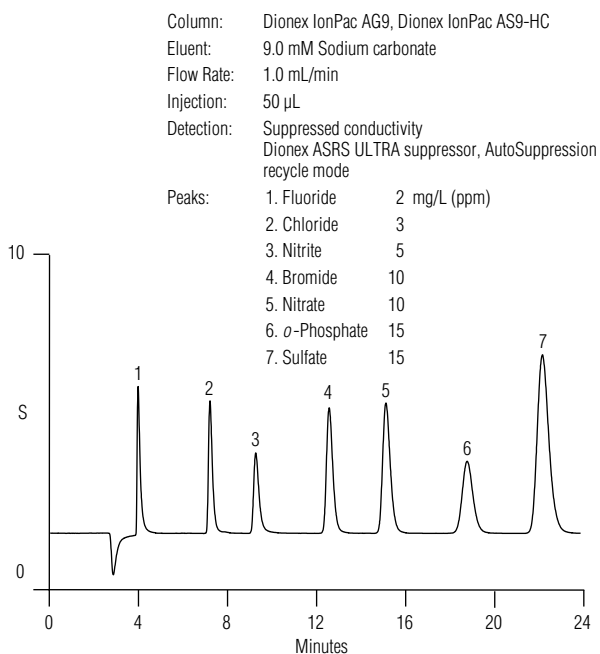


Figure 6. Separation of a low-ppm inorganic anion standard using a Dionex IonPac AS9-HC column.

The method linearity using the Dionex IonPac 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 Dionex IonPac AS9-HC column with a Dionex DX-500 system.

Table 7. Linearity, MDL, retention time, and peak area precision obtained using the Dionex IonPac AS9-HC column^a.

| Anion | Range (mg/L) | Linearity (r^2) | Calculated MDL ^b ($\mu\text{g/L}$) | 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 $\text{NO}_2\text{-N}$) | < 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 $\text{NO}_3\text{-N}$) | 0.13% | 0.23% |
| <i>o</i> -Phosphate | 0.1–100 | 0.9972 | 31.1 (10.2 as $\text{PO}_4\text{-P}$) | 0.08% | 0.75% |
| Sulfate | 0.2–200 | 0.9967 | 14.4 | 0.08% | |

^a Dionex DX-500 system

^b $\text{MDL} = \sigma \cdot t_{\alpha, n-1}$ where $t_{\alpha, n-1} = 3.14$ for $n = 7$

^c RSD = Relative standard deviation, $n = 7$

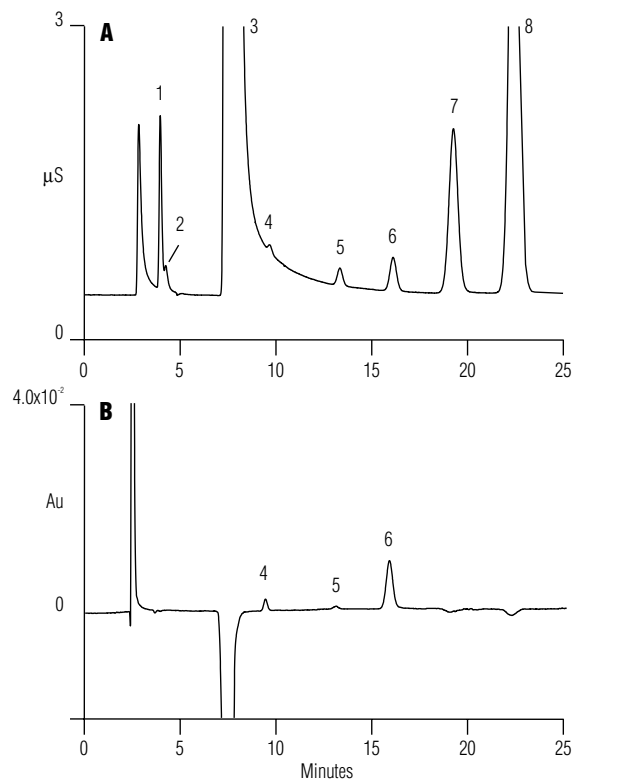
The performance of the Dionex IonPac AS9-HC column was also validated through single-operator precision and bias studies on spiked samples. Table 8 shows typical recovery results for single-operator data obtained using the Dionex IonPac AS9-HC column for common anions spiked into industrial wastewater, 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 Dionex IonPac AS9-HC column.

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 Dionex IonPac 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 Dionex IonPac 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 Dionex IonPac AS14 and Dionex IonPac AS9-HC columns using conductivity and direct UV detection. Note that the ratio is stated with nitrite expressed as both NO_2 and $\text{NO}_2\text{-N}$.

Table 8. Anion recoveries for spiked water samples obtained using the Dionex 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 |
| <i>o</i> -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 |
| <i>o</i> -Phosphate | 20 | 103.5 | 20 | 104.9 | 10 | 84.3 |
| Sulfate | 40 | 81.4 | 40 | 107.5 | 40 | 110.5 |

| | | | | | |
|------------|--|------------------------|----------|----------|------------|
| Column: | Dionex IonPac AG9-HC, Dionex IonPac AS9-HC | Peaks: | A | B | |
| Eluent: | 9.0 mM Sodium carbonate | 1. Fluoride | 1.14 | — | mg/L (ppm) |
| Flow Rate: | 1.0 mL/min | 2. Acetate | — | — | |
| Injection: | 25 μ L | 3. Chloride | 2000 | — | |
| Detection: | A) Suppressed conductivity Dionex ASRS ULTRA suppressor, AutoSuppression recycle mode | 4. Nitrite | 0.14 | 0.18 | |
| | B) UV at 214 nm | 5. Bromide | 0.82 | 0.79 | |
| | | 6. Nitrate | 1.47 | 1.58 | |
| | | 7. <i>o</i> -Phosphate | 21.1 | — | |
| | | 8. Sulfate | 30.3 | — | |



15914

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

Table 9. Maximum Cl:NO₂ ratios at which nitrite can be quantified using the Dionex IonPac AS14 and Dionex 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 μ L injection

Summary

The Dionex 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 Dionex IonPac 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 Dionex 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 Dionex IonPac AS14 column the most appropriate choice for the routine determination of inorganic anions in typical, moderate ionic strength domestic and industrial wastewater samples. The Dionex IonPac AS9-HC column has a significantly higher capacity than the Dionex IonPac AS4A-SC and Dionex IonPac 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.

References

1. Fed. Regist. 1999; Vol. 64, No. 230, 67449.
2. Fed. Regist. 1995; Vol. 60, No. 201, 53988.
3. "The Determination of Inorganic Anions in Water by Ion Chromatography"; U.S. Environmental Protection Agency Method 300.0; Cincinnati, Ohio, 1993.
4. Greenberg, A. E.; Clesceri, L. S.; Eaton, A. D., Eds.; Standard Methods for the Examination of Water and Wastewater, 18th ed.; Am. Public Health Assoc.: Washington, DC, 1992.
5. "Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography"; D4327-97; American Society for Testing and Materials: West Conshohocken, Pennsylvania, 1999; Vol. 11.01, p 420-427.
6. Jackson, P.E.; Haddad, P.R.; Dilli, S. "The Determination of Nitrate and Nitrite in Cured Meats Using High Performance Liquid Chromatography." J. Chromatogr., 1984, 295, 471-478.
7. Pohl, C.A.; Stillian, J.R.; Jackson, P.E. "Factors Controlling Ion-Exchange Selectivity in Suppressed Ion Chromatography." J. Chromatogr., 1997, 789, 29-41.
8. Jackson, L.K.; Joyce, R.J.; Laikhtman, M.; Jackson, P.E. "Determination of Trace Level Bromate in Drinking Water by Direct Injection Ion Chromatography." J. Chromatogr., 1998, 829, 187-192.
9. "Standard Practice for Preparation of Substitute Wastewater"; D5905-98; American Society for Testing and Materials: West Conshohocken, Pennsylvania, 1999; Vol. 11.01, p 782-784.

www.thermoscientific.com/chromatography

©2014 Thermo Fisher Scientific Inc. All rights reserved. ISO is a trademark of the International Standards Organization. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.



| | | | |
|--|---------------------------------------|--------------------------------------|-------------------------------------|
| Africa +43 1 333 50 34 0 | Denmark +45 70 23 62 60 | Japan +81 6 6885 1213 | Russia/CIS +43 1 333 50 34 0 |
| Australia +61 3 9757 4300 | Europe-Other +43 1 333 50 34 0 | Korea +82 2 3420 8600 | Singapore +65 6289 1190 |
| Austria +43 810 282 206 | Finland +358 9 3291 0200 | Latin America +1 561 688 8700 | Sweden +46 8 556 468 00 |
| Belgium +32 53 73 42 41 | France +33 1 60 92 48 00 | Middle East +43 1 333 50 34 0 | Switzerland +41 61 716 77 00 |
| Brazil +55 11 3731 5140 | Germany +49 6103 408 1014 | Netherlands +31 76 579 55 55 | Taiwan +886 2 8751 6655 |
| Canada +1 800 530 8447 | India +91 22 6742 9494 | New Zealand +64 9 980 6700 | UK/Ireland +44 1442 233555 |
| China 800 810 5118 (free call domestic) 400 650 5118 | Italy +39 02 950 591 | Norway +46 8 556 468 00 | USA +1 800 532 4752 |

Thermo
SCIENTIFIC

A Thermo Fisher Scientific Brand