DIONEX

Technical Note 48

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Determination of Trace Anions in High-Purity Water by High-Volume Direct Injection with the EG40

INTRODUCTION

The use of high-volume, direct-injection techniques has improved trace anion analysis.[1-3] This approach facilitates sensitivity at the low- to sub-µg/L levels without the use of a concentrator column or loading pump and valve. Columns and suppressor are used in the microbore format (2 mm) because of the fourfold increase in mass sensitivity over the standard (4 mm) format. Injection volumes are in the range of 1 mL.

This Technical Note describes the use of the EG40 Eluent Generator with the high-volume direct-injection technique to determine trace anions in high-purity waters. The ability to generate high-purity and carbonate-free eluents on-line improves performance for trace-level analysis. Retention time reproducibility is improved, especially for early-eluting species, when using the EG40 eluent generator. The baseline shift from the hydroxide gradient is significantly reduced as well.

Two different columns are described: the 2-mm IonPac® AS11 and the 2-mm AS15. Common inorganic anions and low molecular weight organic acids are determined below µg/L (ppb) levels in less than 35 min. Both methods can also be used with manually prepared hydroxide eluents. (For more information see the *Installation and Troubleshooting Guide* for the IonPac AS11 or AS15.)

EQUIPMENT

Dionex DX-500 Ion Chromatography System consisting of:

GP50 Gradient Pump, microbore configuration

CD20 Conductivity Detector

LC30 Chromatography Enclosure equipped with Rheodyne Model 9126 injector, PEEK, rear-loading (P/N 52291)

EG40 Eluent Generator System with EluGen™ EGC-KOH cartridge

Pressurized Sample Vessel (P/N 37460) and Low-Pressure 3-Way Double Stack Valve (P/N 45009), optional

Plastic bottle assemblies, 4 L, two (for ASRS® external water mode)

300 cm of green 0.75-mm (0.030-in.) PEEK tubing to make a 1000-µL sample loop

PeakNet Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water (DI H_2O), Type I reagent grade, 17.8 MΩ-cm resistance or better

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

Sodium hydroxide 50% w/w aqueous solution (Fisher Scientific)

Potassium hydroxide 45% w/w aqueous solution (Fisher Scientific) optional instead of sodium hydroxide

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 ULICC-004)

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

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

CONDITIONS

Method 1 — **AS11**

Columns:	IonPac AS11 Analytical, 2 x 250 mm (P/N 44077) IonPac AG11 Guard, 2 x 50 mm (P/N 44079)
Trap Columns:	ATC-1 Trap, 4 mm (P/N 37151) ATC Trap, 2 mm (P/N 43131)
Eluent :	Potassium hydroxide (EG40 as the source)
Temperature:	Ambient
EG40 Offset volume:	0 µL

Pump program:

Time (min)	Flow (mL/min)	A (%)	Valve	EG40 Conc. (mM)	Comments
Initial	0.50	100	Load	40.0	40 mM KOH
0	0.50	100	Load	0.5	Load sample loop, Equilibrate 0.5 mM KOH for 7 min
7.00	0.50	100	Inject	0.5	Inject
9.50	0.50	100	Inject	0.5	0.5–5.0 mM KOH in 3.5 min
13.00	0.50	100	Inject	5.0	5.0–26 mM KOH in 14 min
27.00	0.50	100	Inject	26.0	26 mM KOH
27.10	0.50	100	Inject	40.0	40 mM KOH

Detection:	Suppressed conductivity, ASRS-ULTRA, AutoSupression® external water mode
Current setting:	100 mA
Expected Background Conductivity:	1 µS (26 mM KOH)
Expected System Backpressure:	13.8 MPa (2000 psi)
Sample Volume:	1 mL

Method 2 — **AS15**

Columns:	IonPac AS15 Analytical, 2 x 250 mm (P/N 53941) IonPac AG15 Guard, 2 x 50 mm (P/N 53943)
Trap Columns:	ATC-1 Trap, 4 mm (P/N 37151) ATC Trap, 2 mm (P/N 43131)
Eluent :	Potassium hydroxide (EG40 as the source)
Temperature:	30 °C
EG40 Offset volume:	0 µL

Pump program:

Time (min)	Flow (mL/min)	A (%)	Valve	EG40 Conc. (mM)	Comments
Initial	0.50	100	Load	60	60 mM KOH
0	0.50	100	Load	8	Load sample loop, Equilibrate 8 mM KOH initial eluent
5.00	0.50	100	Load	8	End equilibration
5.10	0.50	100	Inject	8	Inject
11.00	0.50	100	Inject	8	Begin gradient to 60 mM
22.00	0.50	100	Inject	60	End gradient
35.00	0.50	100	Load	60	

Detection:	Suppressed conductivity, ASRS-ULTRA, AutoSupression external water mode
SRS Current setting:	100 mA
Expected Background Conductivity:	1.5 µS (60 mM KOH)
Expected System Backpressure:	17.2 MPa (2500 psi)
Sample Volume:	1 mL

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solutions

Stock anion standard solution (1000 mg/L)

Several of the analytes of interest have 1000-mg/L ion standard solutions available from Dionex or other commercial sources. In cases where 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 Amounts of Compounds Used to Prepare 1 L of 1000-mg/L Ion Standards

Anion	Compound	Mass (g)
F^-	Sodium fluoride (NaF)	2.210
$C_2H_3O_3^-$	Glycolic acid ($C_2H_4O_3$)	1.000
CH_3COO^-	Sodium acetate ($CH_3COONa{\cdot}3H_2O$)	2.305
$HCOO^-$	Sodium formate (HCOONa)	1.511
Cl^-	Sodium chloride (NaCl)	1.648
NO_2^-	Sodium nitrite ($NaNO_2$)	1.499
SO_4^{2-}	Sodium sulfate (Na_2SO_4)	1.522
$C_2O_4^{2-}$	Sodium oxalate ($Na_2C_2O_4$)	1.479
NO_3^-	Sodium nitrate ($NaNO_3$)	1.371
PO_4^{3-}	Potassium phosphate, monobasic (KH_2PO_4)	1.433

Composite Standard Solution

Composite standards at lower analyte concentrations are prepared from the 1000-mg/L standards above. Select a range similar to the expected analyte concentrations in the samples. Working standards containing less than 100-µg/L anions should be prepared daily.

ATC Regeneration Solution

2 M Sodium hydroxide

Dilute 160 g of 50% (w/w) sodium hydroxide with degassed, deionized water (having a specific resistance of 17.8 MΩ-cm or greater) to a final weight of 1080 g in an eluent bottle. Avoid the introduction of carbon dioxide from air. (Note: 2 M potassium hydroxide can be used instead of 2 M sodium hydroxide. Preparation is the same as above except that 249 g of 45% potassium hydroxide is used for a final weight of 1090 g.)

SYSTEM PREPARATION AND SETUP

This section describes the procedure for the initial installation and startup of the ASRS-ULTRA, ATCs, and EluGen cartridge. Prepare the ASRS for use by hydrating the eluent chamber with 0.2 N H_2SO_4 and the regen chamber with deionized water. Let the ASRS rest for at least 20 min before pumping eluent through the eluent chamber. (For more information on ASRS operation, consult the *Quickstart Instructions for the ASRS-ULTRA*, Document No. 031368.)

Prepare the ATCs for use by rinsing with 200 mL of 2 M KOH or 2 M NaOH at 2.0 mL/min. This can be done off-line without the GP50 by pressurizing an eluent bottle with helium at 34.5 kPa (5 psi). Then rinse the two ATCs with deionized water at 2.0 mL/min for 20 min. Install the EGC-OH EluGen cartridge according to the instructions in the Operator's Manual for the EG40 Eluent Generator System, Document No. 031373.- Place the 4-mm ATC between the GP50 outlet and the EGC KOH cartridge inlet and the 2-mm ATC between the EG40 degas unit outlet and the injection valve inlet, as shown in Figure 1.

Configure the pressurized water reservoirs as shown in Figure 2 for supplying water to the regen port of the ASRS. It is advisable to use two 4-L bottles plumbed in tandem to ensure uninterrupted external water delivery. Fill the reservoirs with deionized water with a specific resistance of 10 MΩ-cm or greater. (For more information on the operation of the suppressor, refer to the *Installation and Troubleshooting Guide for the ASRS*, Document No. 031367.)

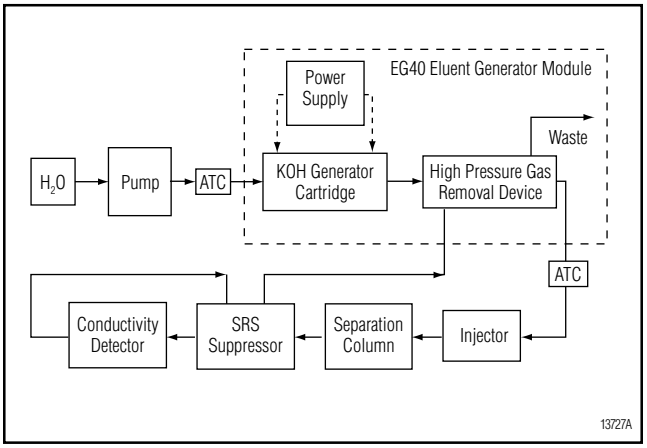

Figure 1. An ion chromatography system with an EG40 eluent generator.

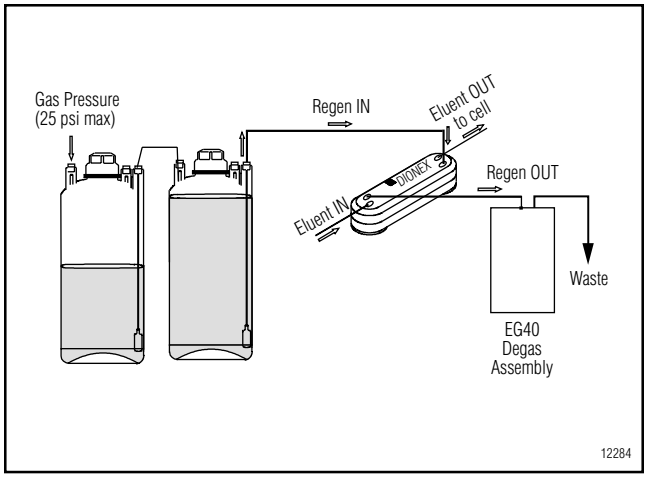

Figure 2. AutoSuppression external water mode using the pressurized water delivery system.

Make a 1000-µL sample loop by cutting a 220-cm portion of green 0.75-mm (0.030-in.) i.d. PEEK tubing. In those cases where a different loop or tubing with a different internal diameter is desired, refer to Table 2 to calculate the length needed. The volume of a loop can be verified by measuring the weight difference between the sample loop filled with deionized water and the empty loop. The inside diameter of tubing varies by as much as 20% (for example, 0.010 ± 0.002 in.).

Connect the columns and suppressor in the IC system by using 0.005-in. (0.125-mm) tubing. Keep the lengths of connecting tubing as short as possible to minimize system void volume. This will ensure efficient 2-mm column operation. Carefully use a razor blade or plastic tubing cutter to ensure that the surfaces of the tubing cuts have straight and smooth surfaces. Irregularity on the surface of a tubing end can result in unwanted additional dead volume.

Table 2 Volume Per Unit Length for Various Tubing Internal Diameters

Material	Color	Internal Diameter		Estimated Volume (µL/cm)
		Inches	Millimeters	
PEEK	Red	0.005	0.125	0.126
"	Black	0.010	0.250	0.506
"	Orange	0.020	0.500	2.022
"	Green	0.030	0.750	4.550

SYSTEM OPERATION

Adjust the reservoir pressure from 0 to 172 kPa (0 to 25 psi) to deliver external water regenerant of 5–7 mL/min before applying current to the ASRS. Ensure that the cap of the reservoir is sealed tightly. Verify that water is flowing out of the Regen Out port without the presence of bubbles. Turn the power on to supply current to the ASRS; the flow rate will drop to about 0.7 mL/min due to gas formation in the regenerant. Check to see that bubbles are forming in the ASRS to verify that water from the regenerant channels is being electrolyzed.

Turn flow on the gradient pump to begin the flow of eluent through the system. If the system backpressure is below 14 MPa (2000 psi), then a portion of the yellow PEEK 0.003-in. (0.075-mm) tubing should be added between the outlet of the degas assembly in the EG40 and the inlet of the injection valve. Confirm that there are no leaks anywhere in the chromatographic pathway. (For more information consult the Operator's Manual for the EG40 Eluent Generator System, Document No. 031373.)

Turn on the EG40 to deliver the highest eluent concentration required by the method using the Run program of PeakNet. Rinse the 2-mm ATC and the separation columns for 30 min at the method flow rate. For the AS15 method, allow the LC30 oven to stabilize at the 30 ˚C operating temperature. The AS11 method is operated at ambient temperature. Assess the quality of the blank by measuring the short-term noise. Use the Autothreshold window of the Optimize module of PeakNet. In a representative 1-min level portion of the chromatogram, a “peak-to-peak” measurement should be less than 5 nS.

It will take at least 4 h for the system to equilibrate to a stable background conductivity for trace analysis. Figure 3 shows a chromatogram of the total background conductivity over time for the AS11 method operating at 38 mM KOH. The system was restarted after having been idle for several days. At times there will be brief increases in conductivity that will minimize upon further operation of the system. It is therefore a good practice to run a system overnight to equilibrate prior to using it the following day.

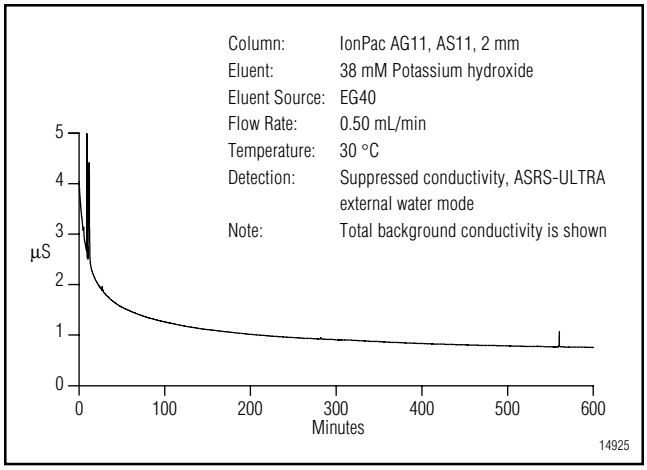

Figure 3. Equilibration time for an EG40 system.

The sample is loaded with either a syringe or a pressurized reservoir. When using a syringe, avoid contaminating the sample. The black rubber plunger in disposable plastic syringes can be a source of significant contamination. To avoid contamination, the syringe should be used to pull sample into the loop when placed at the waste port as shown in Figure 4. Avoid the introduction of air bubbles by applying a slow and steady pull on the syringe. When loading sample with a pressurized reservoir, a low-pressure double-stack valve at the waste port regulates when the sample is loaded into the loop as shown in Figure 5. An AS40 or AS50 autosampler is not suitable for the determination of anions at concentrations below 10 µg/L (ppb). The liquid pathway of the autosampler contributes to anionic contamination.

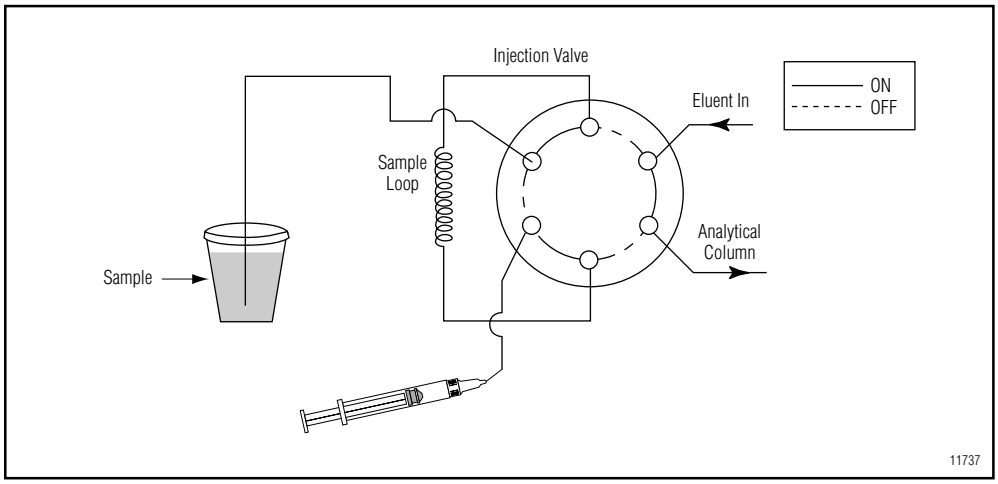

Figure 4. Direct injection sample loading by syringe.

Use commercially available 1000-mg/L ion standards or prepare standards using the information in Table 1. It is recommended to make a 100-mL final volume of 1000-mg/L stock standards in 125-mL high-density polyethylene (HDPE) containers. From this stock standard, make a 1-mg/L dilute standard. Take aliquots from this dilute standard to make working standards in the high-ng/L (ppt) to low-µg/L (ppb) range. Stock standards are stable for at least one month when stored in a refrigerator at 4 °C. Dilute stock standards at the low-mg/L (ppm) levels should be prepared fresh weekly. Working standards at the low-µg/L (ppb) range should be made fresh daily.

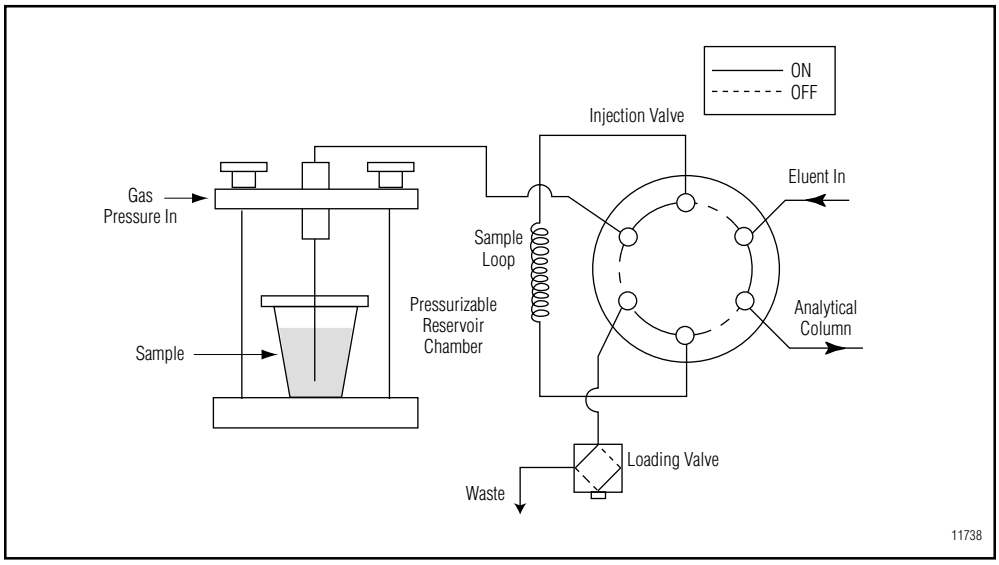

Figure 5. Direct injection sample loading with a pressurizable reservoir chamber.

DISCUSSION AND RESULTS

The EG40 Eluent Generator electrolytically produces high-purity potassium hydroxide (KOH) eluents using deionized water as the carrier stream.[4] The programmable current determines the concentration of the KOH. A KOH cartridge in the EG40 contains K^+ ion electrolyte solution and a KOH generation chamber connected by a cation-exchange connector. The EG40 can generate eluents that are free of carbonate contamination. For gradient separations, the EG40 yields negligible baseline shifts with greater retention time reproducibility. Carbonate-free eluents result in lower background conductivity, providing the best signal-to-noise ratio. These features enhance method performance at trace levels.[5]

Two different hydroxide selective columns are used in this Technical Note: the IonPac AS11 and the IonPac AS15. Both columns are well-suited to trace-level analysis by large-loop injection with a hydroxide gradient. Both columns separate low molecular weight organic acids from fluoride. The capacity of the AS11 and AS15 are 11.25 µeq/column and 56.25 µeq/column, respectively. The higher capacity of the AS15 would allow injection of more concentrated samples without overloading. The resin particle diameters for the AS11 and AS15 are 13 µm and 11 µm, respectively. As a result, the AS11 will operate at lower pressures.

The columns and suppressor used in this method are in the microbore format (2 mm). Microbore chromatography yields a fourfold enhancement in sensitivity compared to separation in the 4-mm standard bore format. This results in less time required for sample loading and is ideal for limited sample volumes. The slower flow rates result in reduced mobile phase consumption. Use of the EG40 further enhances stable performance by delivering reproducible eluents.

The external water mode was chosen for supplying the regenerant solution (i.e., deionized water) to the ASRS because this mode is more effective than the recycle mode at reducing detector noise. A DS-3 detection stabilizer minimizes the effects of cell drift and temperature fluctuations.

Method Performance: IonPac AS11

The AS11 begins with an eluent concentration of 0.5 mM KOH to elute the weakly retained ions such as fluoride and acetate. A gradient from 0.5 mM to 26 mM KOH is used to separate the more strongly retained ions such as phosphate and sulfate. This method is operated at ambient temperature. Figure 6 shows a standard of the ten anions of interest at low- to sub-µg/L levels.

The large peak early in the chromatogram is due to the pressure change of the large loop being placed in-line with the pump. The system void corresponds to the time required for the contents of the 1-mL sample loop to pass through the chromatographic system. Fluoride (4.28 min) is well-resolved from the system void. Acetate partially coelutes with fluoride under these conditions. The large peak at 11.63 min is carbonate.

At the higher eluent concentration, sulfate, oxalate, and phosphate are separated. The chromatographic baseline shift is less than 75 nS because the EG40 produces carbonate-free KOH eluent. The baseline shift would be much higher for this method (800 to 1000 nS) if manually prepared hydroxide eluents were used. The EG40 produces a lower baseline shift for gradient methods, resulting in improved and reliable quantification.

A representative blank for this method is shown in Figure 7. Acetate and formate as well as trace levels of fluoride, oxalate, and phosphate were found from the laboratory point-of-use deionized water system. Determining a blank establishes a starting point above which anion determinations can be made.

Method Performance: IonPac AS15

The IonPac AS15 has performance similar to the AS11, but the operating conditions are different. This method is performed at 30 °C to provide consistent retention time during trace analysis. Figure 8 shows a standard of 11 anions at trace levels. Glycolate is an additional organic acid that can be resolved due to the unique selectivity of the AS15.

The analyte response is higher with the AS11 than with the AS15. This is due to the difference in the properties of the two resins that were used to pack these columns. The AS11 contains a latex-based microporous resin with medium to low hydrophobicity. In contrast, the AS15 contains a grafted macroporous resin with

Column: IonPac AG11, AS11, 2 mm
Eluent: 0.5 mM Potassium hydroxide to 2.5 min to 5.0 mM at 6 min, To 26 mM at 20 min
Eluent Source: EG40
Flow Rate: 0.50 mL/min
Injection: 1 mL
Temperature: Ambient
Detection: Suppressed conductivity, ASRS-ULTRA external water mode

Peaks:

1.	Fluoride	0.32 µg/L
2.	Acetate	2.0
3.	Formate	1.6
4.	Chloride	0.46
5.	Nitrite	0.48
6.	Bromide	0.96
7.	Nitrate	0.30
8.	Carbonate	—
9.	Sulfate	0.31
10.	Oxalate	0.33
11.	Phosphate	1.0

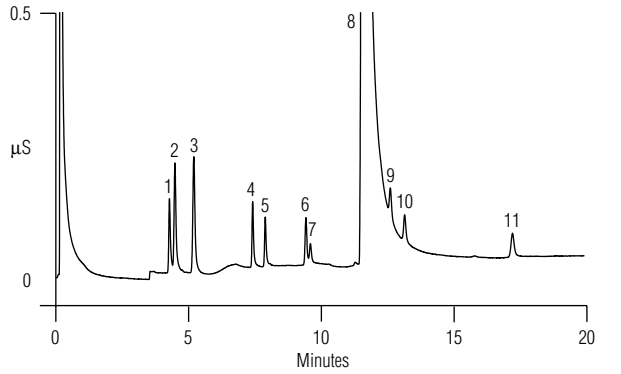

Figure 6. Trace anion determination using the IonPac AS11.

Column: IonPac AG15, AS15, 2 mm
Eluent: 8 mM Potassium hydroxide for 6 min, 6–16 min gradient to 60 mM
Eluent Source: EG40
Flow Rate: 0.50 mL/min
Injection: 1 mL
Temperature: 30 °C
Detection: Suppressed conductivity, ASRS-ULTRA external water mode

Peaks:

1.	Fluoride	0.35	µg/L
2.	Glycolate	0.98	
3.	Acetate	1.5	
4.	Formate	1.3	
5.	Chloride	0.38	
6.	Nitrite	0.46	
7.	Carbonate	—	
8.	Sulfate	0.26	
9.	Oxalate	0.30	
10.	Bromide	0.84	
11.	Nitrate	0.29	
12.	Phosphate	0.80	

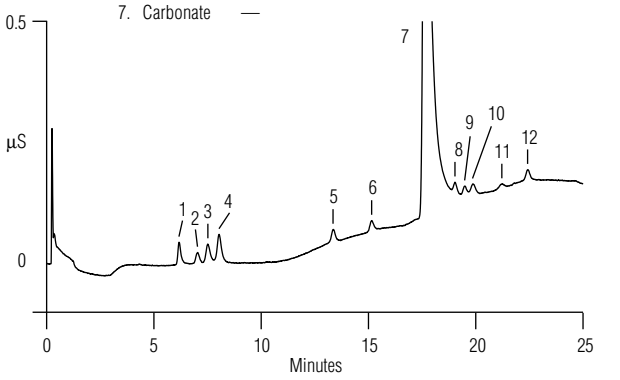

Figure 8. Trace anion determination using the IonPac AS15.

Column: IonPac AG11, AS11, 2 mm
Eluent: 0.5 mM Potassium hydroxide to 2.5 min to 5.0 mM at 6 min, to 26 mM at 20 min
Eluent Source: EG40
Flow Rate: 0.50 mL/min
Injection: 1 mL
Temperature: Ambient
Detection: Suppressed conductivity, ASRS-ULTRA external water mode

Peaks:

1.	Fluoride	0.021	µg/L
2.	Acetate	0.13	
3.	Formate	0.23	
4.	Carbonate	—	
5.	Oxalate	0.031	
6.	Phosphate	0.043	

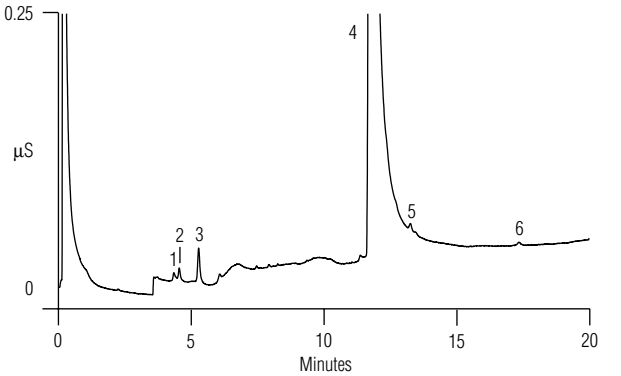

Figure 7. Representative blank for trace analysis using the IonPac AS11.

Column: IonPac AG15, AS15, 2 mm
Eluent: 8 mM Potassium hydroxide for 6 min, 6–16 min gradient to 60 mM
Eluent Source: EG40
Flow Rate: 0.50 mL/min
Injection: 1 mL
Temperature: 30 °C
Detection: Suppressed conductivity, ASRS-ULTRA external water mode

Peaks:

1.	Fluoride	0.046	µg/L
2.	Acetate	0.08	
3.	Formate	0.17	
4.	Chloride	0.093	
5.	Nitrite	0.068	
6.	Carbonate	—	
7.	Nitrate	0.17	

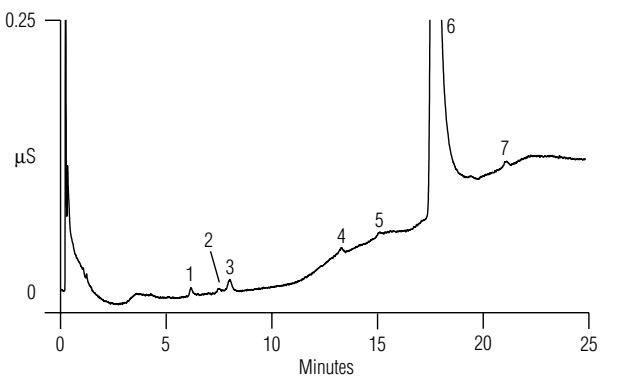

Figure 9. Representative blank for trace analysis using the IonPac AS15.

medium to high hydrophobicity. Grafted resins have a thicker ion-exchange layer, resulting in a longer diffusion layer and, therefore, less efficient peaks.

A gradient from to 8 mM to 60 mM KOH is used to elute the analytes of interest for the AS15. The chromatographic baseline shift is less than 150 nS. This value is higher than the AS11 because the ending eluent concentration is higher (60 mM KOH for the AS15 vs. 26 mM KOH for the AS11).

A representative blank for the AS15 method is shown in Figure 9. As with the AS11 blank, trace amounts of anions were detected. The differences in the anion contents of the two blanks illustrate how trace contamination can affect the blank.

Performance Summary

Method detection limits were established for the anions of interest using both methods and are summarized in Table 3. The standard deviation of seven replicate injections for the lowest level standard was multiplied by the Student's t value for the 99% confidence level.[5] Method detection limits obtained using the AS11 are lower than those obtained using the AS15. Calibration curves were obtained with standards prepared in deionized water using the concentrations listed in Table 4. Results for the anions of interest yielded a linear response with coefficients of determination (r^2) greater than 0.99.

Use of the EG40 resulted in better method performance compared to manually prepared hydroxide eluents. This was demonstrated with a comparison of both techniques for the AS11 method.[6] A standard was prepared with the analytes of interest ranging from 0.1 to 0.3 µg/L. An analysis of 15 replicate injections yielded retention time data as shown in Table 5. Comparable performance for both the EG40 and the manually prepared eluent was observed for later eluting species such as chloride, sulfate, and phosphate. However, a significant difference occurred for weakly retained species such as fluoride, acetate, and formate that are eluted with low concentrations of hydroxide (0.5–5.0 mM). Small variations in carbonate concentration can result in noticeable variations in retention time. This situation is minimized with the EG40 because it can produce hydroxide eluents with no carbonate interference.

Table 3 Method Detection Limits[a] for Anions by High-Volume Direct-Injection Ion Chromatography with the EG40

Anion	AS11 MDL µg/L (ppb)	AS15 MDL µg/L (ppb)
Fluoride	0.0089	0.037
Glycolate	—	0.16
Acetate	0.037	0.14
Formate	0.043	0.11
Chloride	0.0077	0.069
Nitrite	0.013	0.070
Sulfate	0.012	0.061
Oxalate	0.016	0.044
Bromide	0.012	0.060
Nitrate	0.017	0.098
Phosphate	0.029	0.20

[a]Method Detection Limit (MDL) = (SD) x (t_s) 99%, where (t_s) is for a 99% single sided Student's t-test distribution for n= 7

Table 4 Calibration Curve Concentrations (µg/L) for Trace Anion Determination by High-Volume Direct-Injection Ion Chromatography

Method 1 (AS11)			
	Levels		
Anion	**1**	**2**	**3**
Fluoride	0.1	0.3	1.0
Acetate	0.3	1.0	3.0
Formate	0.3	1.0	3.0
Chloride	0.1	0.3	1.0
Nitrite	0.1	0.3	1.0
Bromide	0.3	1.0	3.0
Nitrate	0.1	0.3	1.0
Sulfate	0.1	0.3	1.0
Oxalate	0.1	0.3	1.0
Phosphate	0.3	1.0	3.0
Method 2 (AS15)			
	Levels		
Anion	**1**	**2**	**3**
Fluoride	0.1	0.3	1.0
Glycolate	0.3	1.0	3.0
Acetate	0.3	1.0	3.0
Formate	0.3	1.0	3.0
Chloride	0.1	0.3	1.0
Nitrite	0.1	0.3	1.0
Sulfate	0.3	1.0	3.0
Oxalate	0.3	1.0	3.0
Bromide	1.0	3.0	10.0
Nitrate	0.3	1.0	3.0
Phosphate	1.0	3.0	10.0

CONCLUSION

Use of the EG40 Eluent Generator with either a 2-mm IonPac AS11 or AS15 enables determination of trace anions in high-purity water. It is possible to achieve sub-µg/L detection limits for anions in high-purity water by direct injection. The direct-injection approach is simpler than methods that use a concentrator column and loading pump. Compared to conventional bottle-based hydroxide systems, use of the EG40 improves performance at trace levels.[6]

REFERENCES

1. Kaiser, E.; Riviello, J.; Rey, M.; Statler, J.; Heberling, S. *J. Chromatogr*. **1996**, *739*, 71–79.
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Table 5 Analyte Retention Time Reproducibility Data Using the AS11[a]

Analyte	Spiked Concentration (µg/L)	EG40 Hydroxide Gradient Method (RSD)	Conventional Hydroxide Gradient Method (RSD)
Fluoride	0.1	0.5	4.7
Acetate	0.3	0.5	4.4
Formate	0.3	0.5	1.5
Chloride	0.1	0.4	0.5
Nitrite	0.1	0.4	0.5
Bromide	0.3	0.3	0.3
Nitrate	0.1	0.3	0.3
Sulfate	0.1	0.2	0.2
Oxalate	0.1	0.2	0.2
Phosphate	0.3	0.2	0.2

[a] The analyte retention time reproducibility data were obtained using replicate injections of a sample of 17.8 MΩ-cm DI water spiked with target anions at the concentrations listed. RSD = Standard deviation as a percentage (%) of the mean, n=15.

Table 6 Method Detection Limits (MDLs) for Target Analytes using the AS11[a, b]

Analyte	Spiked Concentration (µg/L)	EG40 Hydroxide Gradient MDL (µg/L)	Conventional Hydroxide Gradient MDL (µg/L)
Fluoride	0.1	0.0089	0.033
Acetate	0.3	0.037	0.085
Formate	0.3	0.043	0.061
Chloride	0.1	0.0077	0.025
Nitrite	0.1	0.013	0.042
Bromide	0.3	0.012	0.023
Nitrate	0.1	0.017	0.029
Sulfate	0.1	0.012	0.022
Oxalate	0.1	0.016	0.030
Phosphate	0.3	0.029	0.099

[a]MDL data were obtained using replicate injections of a sample of 17.8 MΩ-cm DI water spiked with target anions at the concentrations listed. The number of measurements was seven.

[b]The estimated method detection limits were calculated as the standard deviation of the mean measured concentration (n=7) multiplied by 3.143 (the Student's t-value at 99% confidence).

Method detection limit values also show improvement when the EG40 was used. Table 6 summarizes the results for seven replicate injections of the level 1 standard spiked into high-purity water. For all of the ten anions of interest, improvement was observed. This is a result of the lower detection background and minimal baseline shift for the EG40. It is expected that similar performance improvement would be observed with the AS15 or other hydroxide-selective columns when using the EG40 compared to manually prepared hydroxide eluents.

PRECAUTIONS

Special care must be taken when performing trace analysis to minimize contamination. It is very important to use only the highest quality of deionized water. When conducting analyses at trace levels, the sources of contamination are numerous. To minimize contamination, wear disposable, powder-free PVC gloves. Rinse with deionized water after putting them on and air dry. Do not dry with paper towels. All containers should be dedicated to this analysis and rinsed with copious amounts of 17.8 MΩ-cm or better deionized water before use. Exercise caution when handling anything that could have contact with the blank, unknown, or standards. The elements of the chromatographic instrumentation's flow path (eluent containers, injector, pump, valves, tubing, columns, suppressor, and conductivity cell) are all potential sources of contamination. Use caution when switching from a system setup that has previously seen significant concentrations of anions. Rinse with high-purity water to reduce residual contamination.

The ATCs should be periodically regenerated with the procedure described in the “System Preparation and Setup” section. Monitoring the baseline shift during the EG40 hydroxide gradient will indicate when regeneration is necessary. A typical increase for the AS11 and AS15 method should be less than 100 nS and less than 200 nS, respectively. A significant increase beyond these levels would indicate that the ATC has exceeded its capacity to trap ionic contaminants and will need to be regenerated. The frequency of regeneration will depend on the quality of the deionized water and usage rate of the instrument.

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