DIONEX

Application Note 113

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Determination of Trace Anions in High Purity Waters by High Volume/Direct Injection Ion Chromatography

INTRODUCTION

There has been considerable interest in the determination of anions at trace levels by IC. For example, the Electric Power Research Institute (EPRI) has established IC as the analytical technique for determining sodium, chloride, and sulfate down to 0.25 µg/L (ppb) in power plant waters.[1] For high-purity water used in semiconductor processing, the Semiconductor Equipment and Materials International (SEMI) recommends the use of IC for tracking trace ionic contaminants from 0.025 to 0.5 µg/L.[2]

To determine ions from mg/L (ppm) down to mid-µg/L (ppb) levels with IC, a sample size of 10 to 50 µL is sufficient. If lower levels of determination are required, then a preconcentration or trace enrichment technique has typically been utilized.[3,4] With this method, the analytes of interest are preconcentrated on a small precolumn in order to "strip" ions from a measured sample volume. This process concentrates the desired species, resulting in lower detection limits.

However, preconcentration has several disadvantages. Compared with a direct injection method, additional hardware is required, such as a concentrator column used to preconcentrate the ions of interest and a sample pump used for loading the sample. An additional valve is often required for switching the concentrator column in and out of line with the analytical column. Extra time is required for the preconcentration step. Also, analyte loading efficiency can be compromised when additives are present. This occurs because the matrix acts as an eluent for ions that have been retained on the concentrator column.

This application note describes the use of a gradient separation using the IonPac® AS11 column for the determination of trace anions by high volume/direct injection. This method is applicable to high-purity water as well as power plant high-purity waters containing corrosion inhibitors. The instrumentation, techniques, and representative applications of this method are discussed in this application note.

EQUIPMENT

Dionex DX 500 Ion Chromatography System consisting of:
- GP40 Gradient Pump, microbore configuration
- CD20 Conductivity Detector
- LC20 Chromatography Enclosure equipped with Rheodyne Model 9126 injector, converted to six-port valve with valve kit (P/N 45434)

Pressurized Sample Vessel (P/N 37460), optional

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

Low-pressure 3-way double stack valve (P/N 45009), optional

PeakNet Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water (DI H_2O), Type I reagent grade, 18 MΩ-cm resistance or better

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

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

Methanesulfonic acid, >99% pure (Fluka Chemika-BioChemika), optional

EXPERIMENTAL CONDITIONS

Columns:	IonPac AS11 Analytical, 2-mm i.d. (P/N 44077) IonPac AG11 Guard, 2-mm i.d. (P/N 44079) ATC Trap, 2-mm i.d. (P/N 43131)
Eluents:	1) DI H_2O 2) 5 mM NaOH 3) 100 mM NaOH Gradient program—see Table 1.
Flow Rate:	0.5 mL/min
Sample Volume:	750 µL
Detection:	Suppressed conductivity, ASRS 2-mm (P/N 43187), external water mode, 300 mA current

Table 1 Gradient Program

Time (min)	%E1	%E2	%E3	Comments
0	0	65	35	Initial 38 mM NaOH
1.99	0	65	35	End regeneration
2.00	90	10	0	Start 0.5 mM NaOH
9.00	90	10	0	End equilibration
11.50	90	10	0	0.5 mM to 5.0 mM NaOH
15.00	0	100	0	5.0 mM to 26 mM NaOH
29.00	0	78	22	End at 26 mM NaOH
29.10	0	65	35	Step to 38 mM NaOH

Table 2 Masses of Compounds Used to Prepare 1 L of 1000-mg/L Ion Standards

Anion	Compound	Weight (g)
F^-	Sodium fluoride (NaF)	2.210
Cl^-	Sodium chloride (NaCl)	1.648
Br^-	Sodium bromide (NaBr)	1.288
NO_2^-	Sodium nitrite ($NaNO_2$)	1.499
NO_3^-	Sodium nitrate ($NaNO_3$)	1.371
PO_4^{3-}	Potassium phosphate, monobasic (KH_2PO_4)	1.433
SO_4^{2-}	Sodium sulfate (Na_2SO_4)	1.479
$C_2O_4^{2-}$	Sodium oxalate ($Na_2C_2O_4$)	1.522
CH_3COO^-	Sodium acetate ($CH_3COONa \cdot 3H_2O$)	2.305
$HCOO^-$	Sodium formate (HCOONa)	1.511
$CH_3SO_3^-$	Methanesulfonic acid, 99% pure (CH_3SO_3H)	1.010

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solutions

Stock anion standard solution (1000 mg/L)

Prepare 1000-mg/L standards for each of the anions of interest by dissolving the corresponding mass of the salt in 1000 mL of deionized water according to Table 2. Standards are stable for at least one month when stored at 4 °C.

Mixed standard solution

Appropriate mixed standards 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.

Eluent Solutions

5.0 mM Sodium hydroxide (Eluent 2)

Weigh 1.00 kg of deionized water into an eluent reservoir bottle. Degas the water for approximately 10 minutes. Tare the bottle and carefully add 0.40 g of 50% sodium hydroxide directly to the bottle. Quickly transfer the eluent reservoir bottle to the instrument and pressurize it with helium.

100 mM Sodium hydroxide (Eluent 3)

Weigh 992 g of deionized water into an eluent reservoir bottle. Degas the water for approximately 10 minutes. Tare the bottle and add 8.00 g of 50% sodium hydroxide directly to the bottle. Quickly transfer the eluent reservoir bottle to the instrument and pressurize it with helium.

200 mM Sodium hydroxide (ATC regeneration solution)

Weigh 984 g of deionized water into an eluent reservoir bottle. Degas the water for approximately 10 minutes. Tare the bottle on the balance and add 16.0 g of 50% sodium hydroxide directly to the bottle. Quickly transfer the eluent reservoir bottle to the instrument and pressurize it with helium.

DISCUSSION AND RESULTS

The weak initial gradient concentration of this method permits increasing the injection volume from the volumes typically used for a 2-mm IC separation. This is illustrated in Figure 1, in which no significant loss in column efficiency was seen as the sample volume was varied from 25 to 750 µL for the same analyte concentration. Note the absence of a large system void that would obscure early eluting analytes. This was minimized because the large

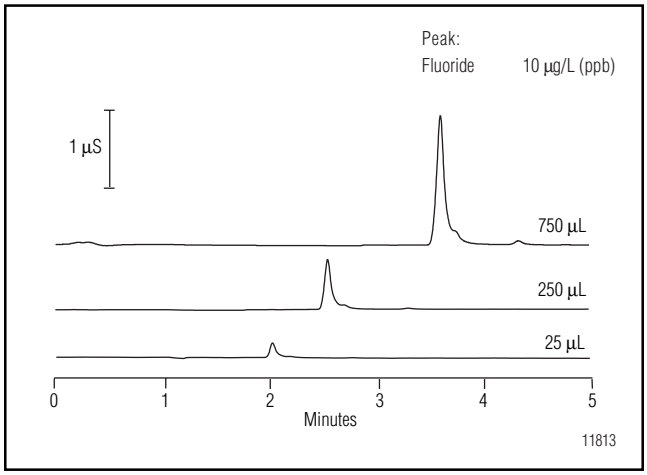

Figure 1 *Increased peak response as sample volume increases.*

aqueous sample was introduced into a mobile phase of low conductivity background (less than 1 µS for 0.5 mM sodium hydroxide).

All columns used in this study are in the microbore (2-mm i.d.) format. This column format has several advantages over the standard 4-mm format. One-quarter the sample volume is required to produce a given response, which results in more convenient and faster loop loading. Also, one-quarter of the eluent is required because the flow can be reduced. This facilitates around-the-clock operation with less frequent eluent changes and thus results in more reproducible chromatography and background conductivity. Overall, the system has improved stability and reliability, thus requiring less operator intervention.

SYSTEM PREPARATION AND SETUP

Prepare the ASRS for use by hydrating the internal membrane. This is accomplished by pumping water or eluent through the suppressor chambers until bubbles are no longer seen. Let the ASRS rest for at least 20 minutes before pumping eluent through the eluent chamber. (For more information on ASRS operation, consult the *Installation Instructions and Troubleshooting Guide for ASRS*, Document No. 034650).

Prepare the ATC (2 mm) for use by flushing with 200 mM sodium hydroxide at a flow rate of 2.0 mL/min. Rinse the ATC with the strongest eluent that will be used during the gradient analysis (38 mM sodium hydroxide). After flushing with eluent, connect the ATC to the eluent line that leads to the injection valve. (For more information on ATC operation, consult the *Installation Instructions and Troubleshooting Guide for the ATC*, Document No. 034535).

Convert the Rheodyne injection valve to a rear loading injector by replacing the standard rotor seal with a three-groove rotor seal. This facilitates loading of the sample into the injection loop with minimal contamination. (For more information see "Conversion of a Rheodyne Front-Loading Injector to a Rear-Loading Injector", Rheodyne Product Note 110).

Make a 750-µL sample loop by cutting a 165-cm (66-in.) portion of 0.030-in. (0.75-mm) i.d. PEEK tubing. In those cases where a different loop or tubing with a different internal diameter is desired, refer to Table 3 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.).

Configure the columns and suppressor into 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.

The sample is loaded either with a syringe or a pressurized reservoir. When using a syringe, take care not to introduce any unwanted contamination by contact of the sample with the syringe. The black rubber plunger in disposable plastic syringes can be a source of significant

Table 3 Volume Per Unit Length for Various Tubing Internal Diameters

Material	Color	Internal Diameter	Volume
PEEK	Red	0.005 in. (0.125 mm)	0.126 µL/cm
PEEK	Black	0.010 in. (0.250 mm)	0.506 µL/cm
PEEK	Orange	0.020 in. (0.500 mm)	2.022 µL/cm
PEEK	Green	0.030 in. (0.750 mm)	4.550 µL/cm

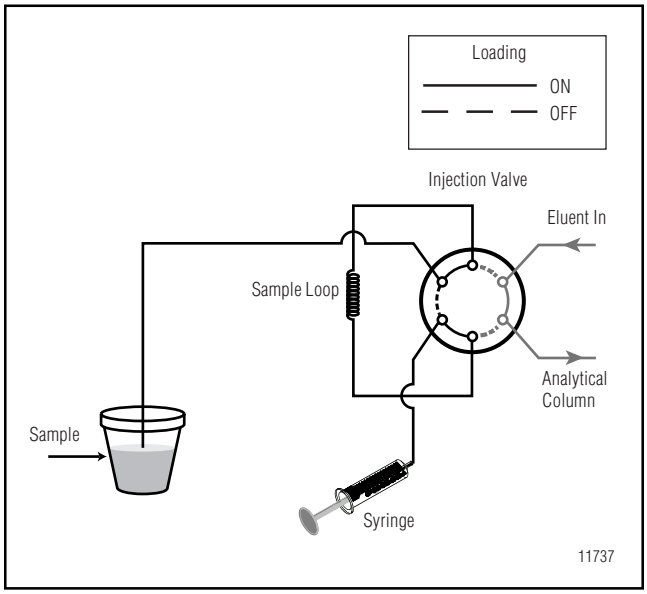

Figure 2 *Direct injection sample loading by syringe.*

contamination. To avoid this, the syringe can be used to pull instead of push sample into the loop when placed at the waste port as shown in Figure 2. Take care not to introduce bubbles into the loop by pulling too hard. The other method for sample loading is with the use of 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 3. An autosampler should not be used for the determination of anions at concentrations below 10 µg/L (ppb).

Configure the pressurized water reservoirs as shown in Figure 4 for supplying water to the regen port of the ASRS. It is advisable to use two 4-L bottles plumbed together to ensure uninterrupted external water delivery. Fill the reservoirs with deionized water with a specific resistance of 10 MΩ-cm or greater. Adjust the reservoir pressure from 0 to 25 psi (0 to 172 kPa) to deliver external water regenerant of 5 to 7 mL/min before applying current. Ensure that the cap of the reservoir is sealed tightly. After the current is applied, the flow rate will drop to about 0.7 mL/min due to gas formation in the regenerant (For more information on the operation of the suppressor, refer to the *Installation and Troubleshooting Guide for the ASRS*, Document No. 034650).

METHOD PERFORMANCE

An important starting point for conducting trace analysis is to establish a blank. This is easily done by injecting high purity deionized water as a sample, using the same set of containers, pipetting devices, and so forth. This establishes baseline anion concentrations above which reliable quantification can be made. Make several replicate injections to establish a precise reading. A representative blank is shown in Figure 5.

A blank will only be as good as the deionized water that is injected and the care taken to minimize contamination during handling. The deionized water used for preparing rinse solution, eluent, and standards should be free of measurable levels of ionic impurities, organics, microor-

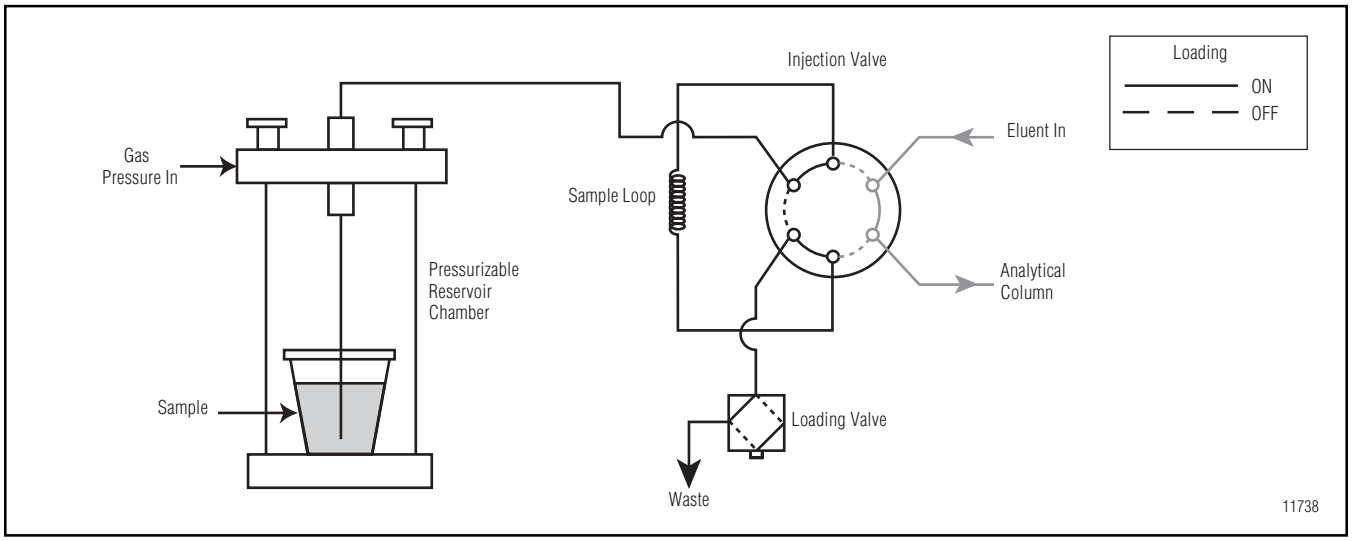

Figure 3 *Direct injection sample loading.*

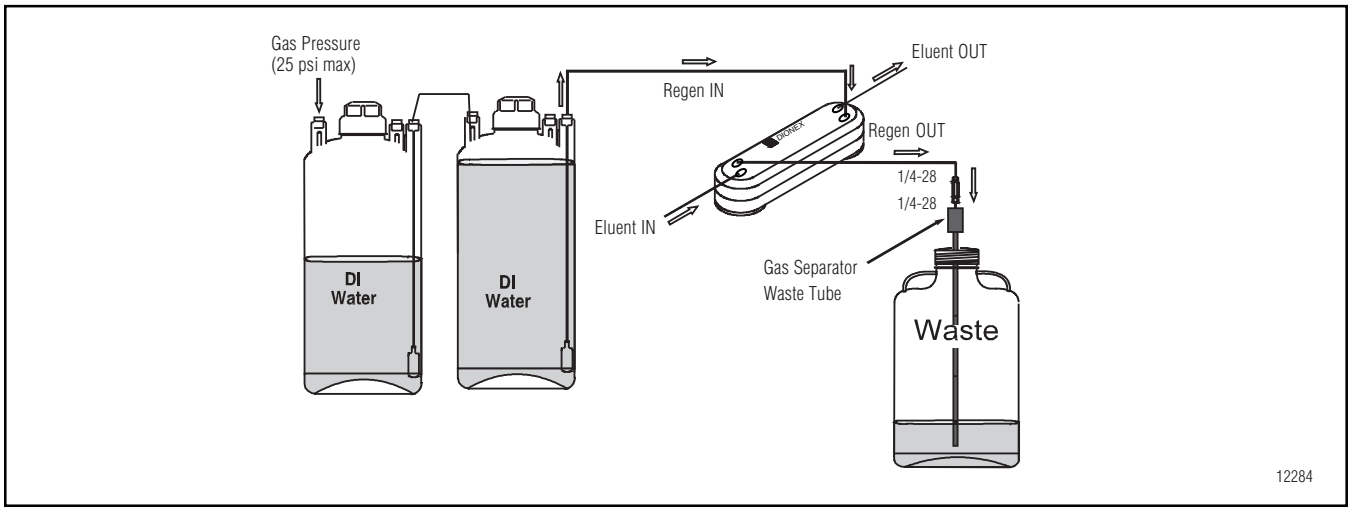

Figure 4 *AutoSuppression™ external water mode using the pressurized water delivery system.*

ganisms, and particulate matter larger than 0.2 µm. Soak containers for at least 24 hours with deionized water and rinse several times prior to use. Wear disposable gloves (for cleanroom electronics applications) when handling apparatus that makes contact with eluent, standard, or samples.

The total baseline shift between the beginning and the end of the gradient analysis should be no more than 1 µS. To ensure this, sodium hydroxide eluents should be prepared with minimal carbonate contamination. In addition, the ATC should be regenerated at the beginning and end of each operational day to remove any contaminants that may have collected on it. This can be readily done by pumping at least 30 mL of 100 mM sodium hydroxide (eluent no. 3) through the ATC.

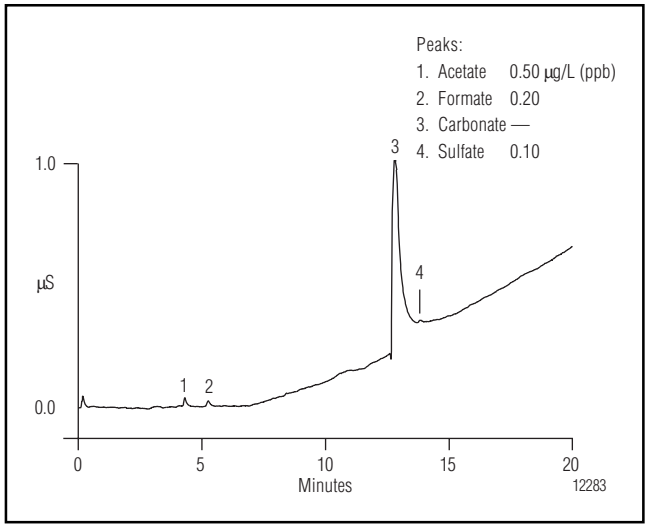

Figure 5 *A representative blank for trace analysis.*

For the best performance at trace levels it is critical that baseline noise be kept to a minimum. From startup, a system typically requires about 5 hours to establish a stable background conductivity. For this reason it is best to keep the system running continuously. Ensure that there is an adequate supply of the eluents, external water, and waste containers to allow the system to run unattended. All moving parts of the gradient pump need to be in good working order (check valves, piston seals, and pistons).

The DX 500 instrumentation and PeakNet software provides the analyst with the ability to monitor baseline noise. In the diagnostic menu under "pressure statistics", the GP40 Gradient Pump displays the measured pressure in psi from the pressure transducer as well as the pressurization point values from the left and right pistons. In a 1-minute segment, the pump pressure reading difference should be less than 20 psi and the pressure point difference should be 5 units or less. In the PeakNet Optimize program, the Auto Threshold function lets the user select a baseline region for noise measurement. In a representative 1-minute section, an equilibrated system in good working order should be able to consistently deliver a noise reading less than 10 nS peak to peak.

Prepare standards using the information in Table 1. It is recommended to make up a 100-mL final volume of 1000-mg/L stock standards in 125-mL high-density polyethylene HDPE containers. From this stock standard, a 1-mg/L dilute standard is made. Take aliquots from this dilute standard to make working standards at the low-µg/L (ppb) down to the high-ng/L (ppt) range.

Stock standards are stable for at least 1 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.

The IonPac AS11 gradient separation was chosen for this method because of its high resolving power for inorganic anions and organic acids. A representative low-level standard for 10 anions in high purity water is shown in Figure 6. The large peak at 14 minutes is carbonate, the size of which will vary with the amount of dissolved carbon dioxide in the sample. The gradient begins with 0.5 mM sodium hydroxide, which permits fluoride to elute after the void volume and resolves acetate and formate as well. Strongly retained polyvalent ions such as sulfate and phosphate elute later as the gradient concentration rises to a final concentration of 26 mM sodium hydroxide. To regenerate the system, the gradient begins with 2 minutes of 38 mM sodium hydroxide.

This method is also applicable to high-purity power plant waters containing corrosion inhibitors. Figure 7 shows a sample of 8-mg/L morpholine containing trace-level anions. No significant difference in peak efficiency or retention time is observed compared to the analysis of deionized water. Method detection limits were established for 10 anions using both deionized water and 8-mg/L morpholine. Using the standard deviation of nine replicate injections multiplied by the Student's *t* value for the 99% confidence level yielded the values summarized in Table 4.

Calibration curves were obtained with standards prepared in deionized water and 8-mg/L morpholine using the concentrations listed in Table 5. Results for the 10 anions of interest yielded a linear response in both matrices with coefficients of determination (r^2) greater than 0.99. Table 6 lists the r^2 values as well as the slopes and intercepts for the ten anions. This statistical analysis showed no evidence of significant bias when comparing the deionized water calibration curve with the one prepared in 8-mg/L morpholine. This fact allows the analyst to quantify unknown anion concentrations in 8-mg/L morpholine (or other amine treated matrix) by using calibration plots based on aqueous standards. Figure 8 shows the calibration curves for chloride prepared in both matrices. Slopes are parallel whereas intercepts differ based on differing blanks.

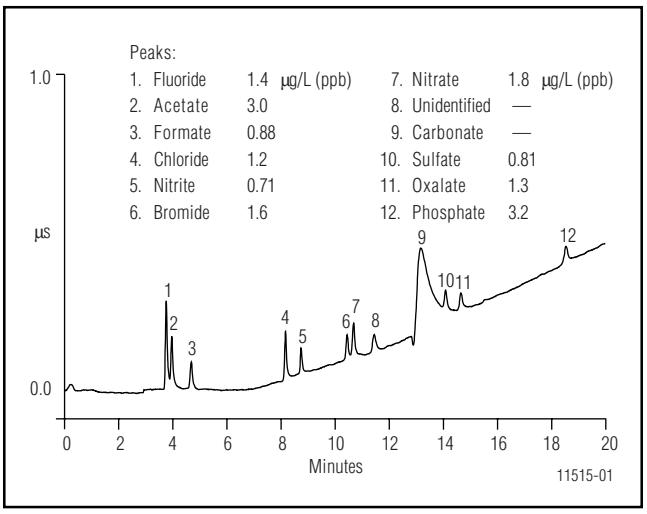

Figure 6 *Trace anion determination.*

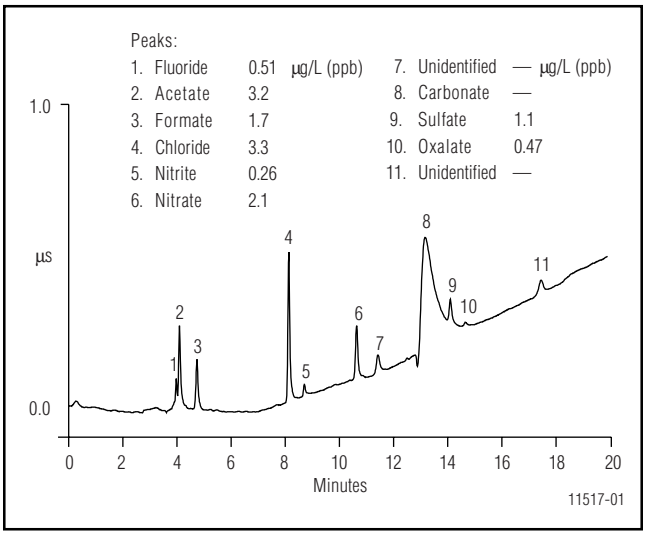

Figure 7 *Trace anion determination in 8-mg/L morpholine.*

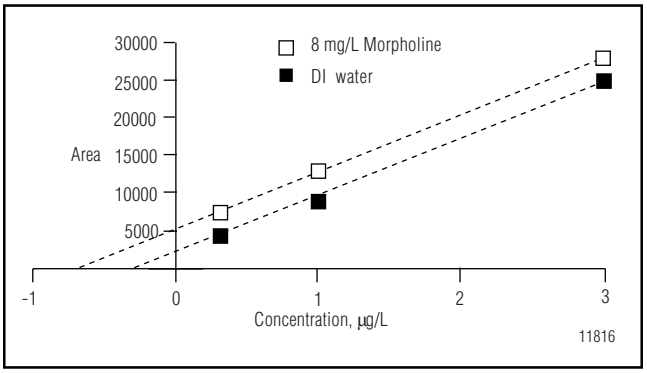

Figure 8 *Calibration curve for chloride in water and 8-mg/L morpholine.*

Table 4 Method Detection Limits for Anions by High Volume Direct Injection/Ion Chromatography

Anion	DI Water MDL[b] [µg/L (ppb)]	Morpholine-Treated Water[a] MDL[b] [µg/L (ppb)]
Fluoride	0.015	0.081
Acetate	0.20	0.86
Formate	0.10	0.55
Chloride	0.035	0.25
Nitrite	0.041	0.24
Bromide	0.084	0.15
Nitrate	0.061	0.13
Sulfate	0.10	0.12
Oxalate	0.058	0.27
Phosphate	0.42	0.82

[a] 8-mg/L Morpholine

[b] MDL = (S.D.) x $(t_s)_{99\%}$, where (t_s) is for a 99% single-sided Student's *t*-test distribution for n=9.

Table 5 Calibration Curve Concentrations (µg/L) for Trace Anion Determination by High Volume Direct Injection/Ion Chromatography

Anion	Level 1	Level 2	Level 3
Fluoride	0.3	1	3
Acetate	1	3	10
Formate	1	3	10
Chloride	0.3	1	3
Nitrite	0.3	1	3
Bromide	1	3	10
Nitrate	0.3	1	3
Sulfate	0.3	1	3
Oxalate	0.3	1	3
Phosphate	1	3	10

PRECAUTIONS

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. Disposable gloves should be worn at all times when handling apparatus that contacts standard or sample. All containers should be dedicated to this analysis and copiously rinsed with 18 MΩ-cm or better deionized water before use. Exercise caution when handling anything that could have contact with the blank, unknown, or standards. The flow path of the chromatographic instrumentation (injector, pump, valves, tubing, eluent containers, columns, suppressor, and conductivity cell) are all potential sources of contamination. Take care when switching from a system setup that had previously seen significant concentrations of anions. Rinse with high purity water to reduce residual contamination.

Table 6 Calibration Curve Parameters for Trace Anion Determination by High Volume Direct Injection/Ion Chromatography

Anion	Parameter	DI Water	Morpholine-Treated Water[a]
Fluoride	r^2	0.9995	0.9983
	Slope	0.0000876	0.0001043
	Intercept	-0.081	-0.201
Acetate	r^2	0.9994	0.9985
	Slope	0.000296	0.000257
	Intercept	-3.43	-3.48
Formate	r^2	0.9979	0.9991
	Slope	0.000153	0.000162
	Intercept	-1.17	-1.39
Chloride	r^2	0.9944	0.9973
	Slope	0.000137	0.000127
	Intercept	-0.207	-0.646
Nitrite	r^2	0.9991	0.9983
	Slope	0.000174	0.000172
	Intercept	-0.00787	-0.508
Bromide	r^2	0.9988	0.9995
	Slope	0.000232	0.000234
	Intercept	0.452	0.354
Nitrate	r^2	0.9967	0.9924
	Slope	0.000197	0.000200
	Intercept	-0.225	-0.225
Sulfate	r^2	0.9878	0.9980
	Slope	0.00020	0.00021
	Intercept	-0.173	-0.370
Oxalate	r^2	0.9934	0.9929
	Slope	0.000304	0.000289
	Intercept	0.123	0.289
Phosphate	r^2	0.9937	0.9927
	Slope	0.000715	0.000889
	Intercept	0.657	0.584

[a] 8 mg/L Morpholine

The methanesulfonic acid anion is useful as an internal standard for the purpose of identifying sources of contamination. Since it is not typically found in DI H_2O blanks, it can be added to the calibration standards to verify system performance without complications from the introduction of trace anion contaminants. Methanesulfonate elutes just after formate under these conditions.

CONCLUSION

Use of a gradient separation on the IonPac AS11 enables low to sub-µg/L detection limits for anions in high-purity water by direct injection. This technique eliminates the sample pump, concentrator column, preconcentration time, and recovery problems associated with sample preconcentration. This method simplifies the analysis and reduces run time of high-purity water and power plant treated waters.

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4. Dionex Corporation. *Technical Note No. 8*, Sunnyvale, CA, **1994**.

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