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APPLICATION NOTE 114

Determination of trace anions in high-purity waters using direct injection and two-step isocratic ion chromatography

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Keywords
Ion chromatography, IC, acetate, formate, glycolate, carbonate, oxalate, sulfate, chloride, fluoride, Dionex IonPac AS14, isocratic, morpholine, power plant, phosphate, nitrate, boric acid eluent, sodium hydroxide eluent

Introduction

Reliable methods to quantify anionic contaminants in high-purity water are essential to both the semiconductor and power generation industries. Anionic contamination is known to cause metal corrosion in microelectronic circuitry.[1] Likewise, the presence of low µg/L (ppb) concentrations of chloride and sulfate can make the stainless steel components of a power plant (such as steam generators, boiler tubes, condensor tubes, and turbine blades) susceptible to stress corrosion cracking.[2]

To respond quickly to changing conditions, a fast method is needed by those monitoring anionic contamination at trace levels. This application note describes a rapid, high-volume, direct-injection technique that utilizes a Thermo Scientific™ Dionex™ IonPac™ AS14 2 mm analytical column and a borate eluent with a step change. The separation was applied to high-purity water as well as amine-treated matrices of interest to the power generation industry. Common anions such as fluoride, chloride, nitrate, phosphate, and sulfate were determined at levels below 1 µg/L (ppb) in less than 15 minutes.

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Experimental

Equipment

- Thermo Scientific™ Dionex™ DX 500 Ion Chromatography system* consisting of:
  - GP40 Gradient Pump, microbore configuration
  - CD20 Conductivity Detector with DS3 Conductivity Cell (temperature controlled)
  - LC20 Chromatography Enclosure equipped with a six-port valve with Valve Kit

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system.

- Pressurized Sample Vessel and Low-pressure 3-way Double Stack Valve for pressurized injections, optional 4 L plastic bottle assemblies (two for external water mode)
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

Reagents and standards

- Deionized water (DI H_2O), Type I reagent grade, 18 MΩ·cm resistance or better
- Boric acid, >99% pure (Sigma-Aldrich®)
- Sodium hydroxide, 50% w/w aqueous solution (Fisher Scientific™)
- Sodium and potassium salts, ACS reagent grade, for preparing anion standards (Fisher Scientific)
- Glycolic acid, >99% pure (Fluka®)

Conditions

Columns:	Dionex IonPac AS14 Analytical, 2 × 250 mm (P/N 046129) Dionex IonPac AG14 Guard, 2 × 50 mm (P/N 046138)
Trap Column:	Thermo Scientific™ Dionex™ IonPac™ ATC Trap, 2 mm (Replaced by Dionex IonPac ATC-3, 4 × 35 mm, P/N 079932)
Eluent A:	9 mM Boric acid/ 6.75 mM Sodium hydroxide
Eluent B:	40 mM Boric acid/ 30 mM Sodium hydroxide

Pump Program:

Time	*%A*	*%B*	*Comments*
Initial	100	0	Equilibrate initial eluent
0	100	0	Load sample loop
5.00	100	0	Inject
8.50	100	0	
8.51	0	100	Step to stronger eluent
15.00	0	100	

Eluent Flow Rate:	0.75 mL/min
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ ASRS™ (2 mm), AutoSuppression™ external water mode SRS Current Setting: 300 mA
Expected Background Conductivity:	2–4 µS
Expected System Backpressure:	17.2 MPa (2,500 psi)
Sample Volume:	1 mL

Preparation of solutions and reagents

Standard solutions

Stock anion standard solution (1,000 mg/L)

Prepare 1,000 mg/L standards for each of the anions of interest by dissolving the corresponding mass of the dried salt in deionized water to a final volume of 1,000 mL 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 liter of 1,000 mg/L ion standards.

Anion	Compound	Mass (g)
F^-	Sodium fluoride (NaF)	2.210
Cl^-	Sodium chloride (NaCl)	1.648
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
$C2O_4^{2-}$	Sodium oxalate ($Na_2C_2O_4$)	1.522
CH_3COO^-	Sodium acetate ($CH_3COONa•3H_2O$)	2.305
$HCOO^-$	Sodium formate (HCOONa)	1.511
$C2H_3O_3^-$	Glycolic acid ($C_2H_4O_3$)	1.013

Mixed standard solution

Appropriate mixed standards are prepared from the 1,000 mg/L standards above. Select a range similar to the expected analyte concentrations in the samples. Working standards of concentrations less than 100 µg/L should be prepared daily.

Eluent solutions

Stock eluent solution: 200 mM boric acid/150 mM sodium hydroxide

Dissolve 12.36 g of boric acid in 900 mL of deionized water, add 12.0 g of 50% sodium hydroxide, and dilute to 1.00 L. Transfer this solution to an eluent container and vacuum degas for 5 minutes.

Eluent A solution: 9 mM boric acid/6.75 mM sodium hydroxide

Vacuum degas 955 g of deionized water in a 1 L eluent container for 5 minutes. Add 45 mL of the stock eluent solution. Transfer to the IC.

Eluent B solution: 40 mM boric acid/30 mM sodium hydroxide

Vacuum degas 800 g of deionized water in a 1 L eluent container for 5 minutes. Add 200 mL of the stock eluent solution. Transfer to the IC instrumentation.

Note: Care must be taken to minimize air contact with the eluent; absorbed carbon dioxide will change the eluent characteristics. Keep eluent blanketed with helium or nitrogen gas to prevent atmospheric carbon dioxide from entering.

200 mM sodium hydroxide (regeneration solution)

Weigh 990 g of deionized water into an eluent reservoir bottle. Degas the water for approximately 5 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.

System preparation and setup

Prepare the Dionex ASRS supressor 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 Dionex ASRS suppressor sit for at least 20 minutes before pumping eluent through the eluent chamber. (For more information on operation, consult the *Installation Instructions and Troubleshooting Guide for the ASRS,* Document No. 034650).

Prepare the Dionex IonPac ATC trap column (2 mm) separately by flushing with 200 mM sodium hydroxide at a flow rate of 2.0 mL/min. Rinse with the strongest eluent that will be used during the gradient analysis (40 mM boric acid/ 30 mM sodium hydroxide). After rinsing with eluent, connect the Dionex IonPac ATC trap column to the eluent line that leads to the injection valve. (For more information on 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 1,000 µL sample loop by cutting a 220 cm portion of 0.030 in. (0.75 mm) i.d. PEEK™ tubing. In cases where a 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 dry, empty loop. The inside diameter of tubing varies by as much as 20% (i.e., 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, which will ensure efficient 2 mm column operation. Carefully use a razor blade or plastic tubing cutter so that the surfaces of the tubing cuts have straight and smooth surfaces. Irregularity on the surface of a tubing end can result in unwanted 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 contamination. To avoid this, the syringe should be used to pull instead of push sample into the loop when placed at the waste port as shown in Figure 1. Take care not to introduce bubbles into the loop by pulling too quickly. 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 2. Certain autosamplers are available that are suitable for trace (<10 µg/L) anion analysis. Contact the nearest Thermo Fisher Scientific sales office for more details.

Table 2. Volume per unit length for various tubing internal diameters.

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

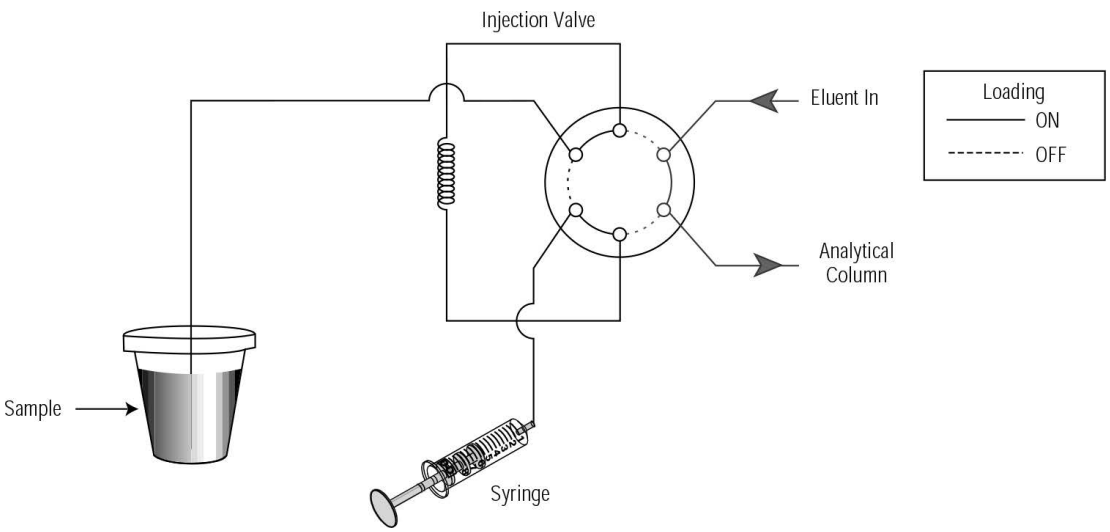

Figure 1. Direct injection sample loading by syringe.

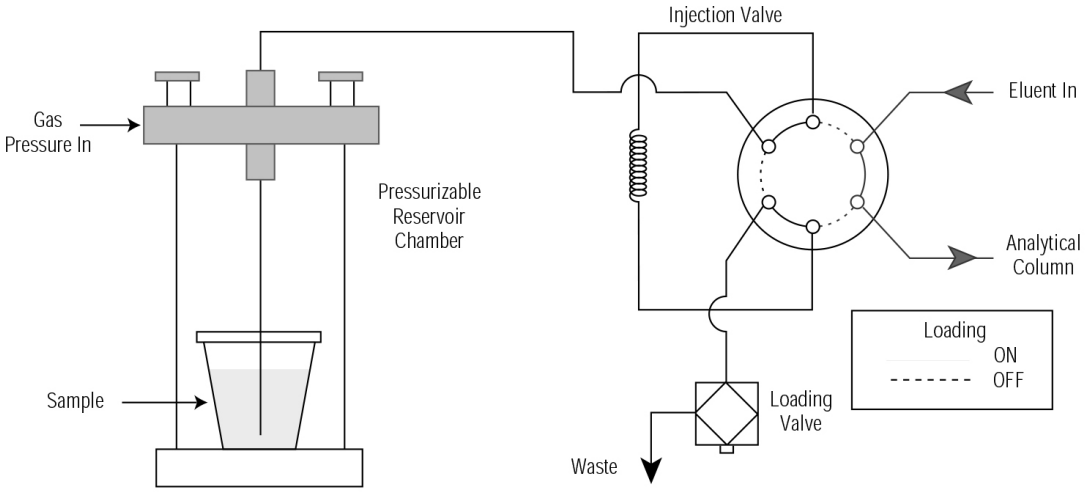

Figure 2. Direct injection sample loading by pressure.

Configure the pressurized water reservoirs as shown in Figure 3 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. Adjust the reservoir pressure from 0 to 172 kPa (0 to 25 psi) 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).

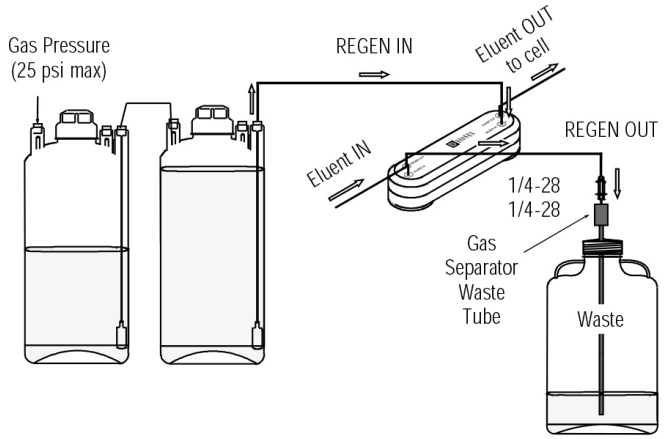

Figure 3. AutoSuppression external water mode using the pressurized water delivery system.

Prepare standards using the information in Table 1. It is recommended to make up a 100 mL final volume of 1,000 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. Prepare calibration standards of three concentrations to correspond to the expected range found in the samples of interest.

Results and discussion

The Dionex IonPac AS14 column quickly resolves inorganic anions such as fluoride, chloride, nitrate, phosphate, and sulfate. Fluoride can be readily quantified because it is retained well out of the system void and is separated from the weakly retained organic acids. This column can be used with a weak borate eluent, making it suitable for a high volume/direct injection technique.

Microbore chromatography yields a four-fold enhancement in sensitivity over the 4 mm separation. This results in less time being required for filling the sample loop and is ideal for limited sample volumes. The slower flow rates result in reduced mobile phase consumption, so the system can be operated with little operator involvement, giving stable performance.

The eluent program starts with a low borate eluent concentration to separate weakly retained ions such as fluoride, glycolate, acetate, and formate. It then steps to a higher concentration to quickly elute more strongly retained ions such as nitrate, phosphate, sulfate, and oxalate. The borate eluent is made by mixing boric acid and sodium hydroxide, which results in more consistent eluent quality than the traditional method of dissolving sodium tetraborate in water. The ratio of boric acid to sodium hydroxide was optimized to obtain the best resolution of carbonate from chloride.

Conditions were optimized to yield a fast run time with minimal baseline noise. The run time of the separation was decreased by selecting a flow rate of 0.75 mL/min. No significant loss in column efficiency was observed. To achieve sensitivity at trace levels the sample volume was increased from one typically employed for a 2 mm separation (50 µL or less) to 1,000 µL. Larger injection volumes may be used, but run times will be extended 1 minute for each additional 0.75 mL. External water regeneration was chosen over the recycle mode because it is more effective at reducing detector noise. A Dionex DS-3 detection stabilizer minimizes the effects of cell drift and temperature fluctuations.

Method performance

A representative standard run as shown in Figure 4 illustrates the features of this separation. The peak at the beginning of the run is due to the pressure upset that the system experiences when the sample loop is switched from Load to Inject. The large system void corresponds to the time required for the sample volume to pass through the chromatographic system. Fluoride is well-resolved from the system void but not baseline resolved from the organic acids (glycolate, acetate, and formate) under these conditions. Nitrate through oxalate are eluted with the higher eluent concentration. The pump program returns to the dilute eluent concentration to equilibrate for 5 minutes prior to the next injection. Depending on the amount of carbonate present in the sample, nitrite and bromide can coelute with carbonate. If quantification of acetate, formate, nitrite, and bromide is important, it is recommended that the high-volume/direct-injection method using the Dionex IonPac AS11 column be used.[3] To resolve fluoride, glycolate, and acetate, the best method is the gradient tetraborate method discussed in the Dionex AS14 column manual (see *Installation and Troubleshooting Guide for the AS14*, Document no. 031199).

		Peaks:			µg/L(ppb)
Column:	Dionex IonPac AS14 Analytical, 2 mm		1. Fluoride	3	
	Dionex IonPac AG14 Guardl, 2 mm		2. Glycolate	—	
Eluent:	6.75 mM NaOH, 9 mM Boric acid,		3. Acetate	—	
	Step to 330 mM NaOH,		4. Formate	—	
	40 mM Boric acid at 3.5 min		5. Chloride	10	
Flow Rate:	0.75 mL/min		6. Carbonate	—	
Inj. Volume:	1 mL		7. Nitrate	10	
Detection:	Suppressed conductivity		8. Phosphate	10	
	Dionex ASRS, AutoSuppression,		9. Sulfate	10	
	external water mode		10. Oxalate	10	

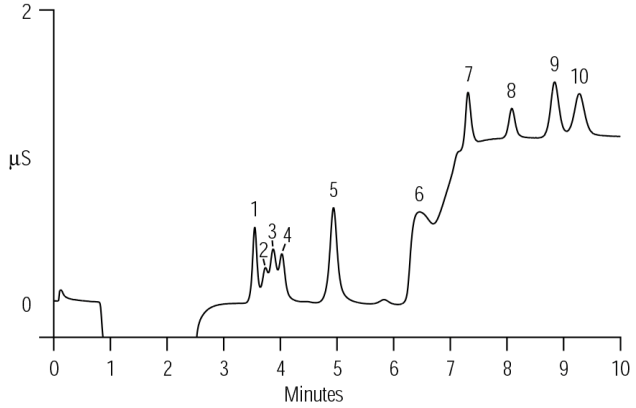

Figure 4. Trace anion standard.

This method is also applicable to high-purity power plant waters containing corrosion inhibitors. Figure 5 shows a sample of 8-mg/L morpholine containing a standard of trace level anions. No significant difference in peak efficiency or retention time is observed compared to the analysis in deionized water. A larger quantity of carbonate was detected but did not interfere with the quantification of chloride.

				µg/L(ppb)
Peaks:	1. Fluoride	3		
	2. Acetate	—		
	3. Formate	—		
	4. Chloride	10		
	5. Carbonate	—		
	6. Nitrate	10		
	7. Phosphate	10		
	8. Sulfate	10		
	9. Oxalate	10		

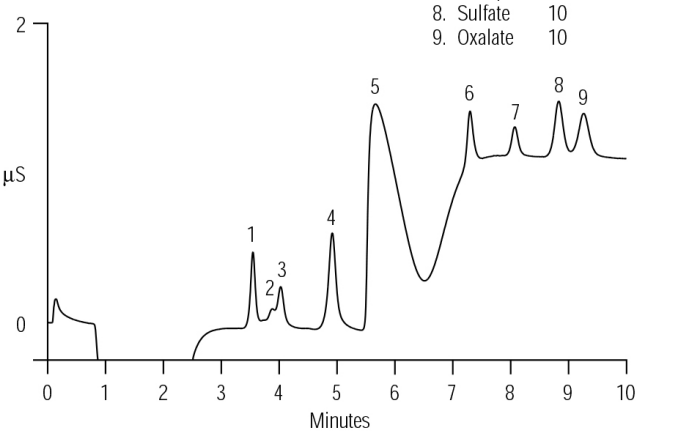

Figure 5. Trace anions in 8 mg/L (ppm) morpholine.

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. A baseline anion concentration is established above which reliable quantification can be made. Make several replicate injections to establish a precise reading. A representative blank (from a typical laboratory point-of-use deionization system) is shown in Figure 6. It is not uncommon to have trace levels of acetate, formate, and sulfate from a typical laboratory point-of-use deionized water unit.

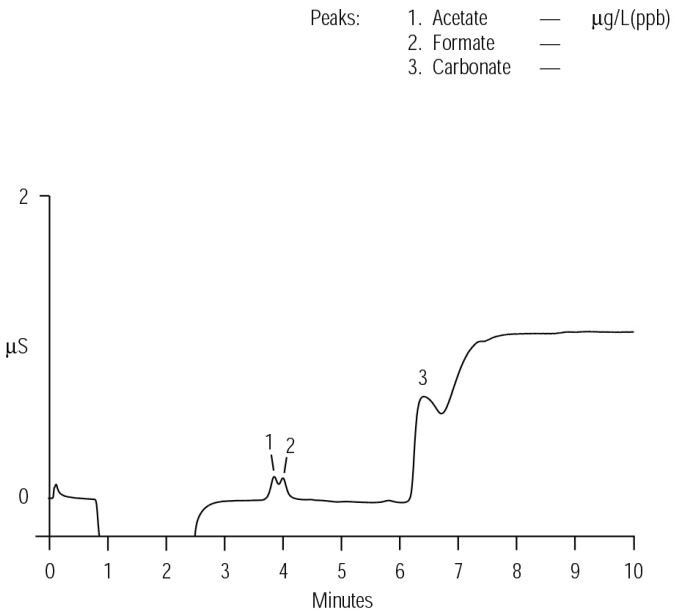

Figure 6. Representative blank for trace analysis.

The total baseline shift between the weak and strong eluent concentration is typically 1.5 µS. Use of the Dionex ATC trap column minimizes the upset that is associated with switching to the higher eluent concentration. The Dionex ATC trap column should be periodically regenerated by pumping at least 30 mL of the concentrated stock eluent solution through it. How often this is necessary will depend on the level of contamination in the deionized water used to prepare the eluent.

For the best performance at trace levels it is critical that baseline noise be kept to a minimum. From startup, a system for trace analysis 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 Dionex DX 500 instrumentation and Dionex PeakNet software provide the analyst with the ability to monitor baseline noise. In the diagnostic menu under “pressure statistics”, the Dionex GP40 Gradient Pump displays the measured pressure from the pressure transducer as well as the pressurization point values from the left and right pistons. In a 1 min segment, the pump pressure reading difference should be less than 138 kPa (20 psi) and the pressure point difference should be 5 units or less. In the Dionex PeakNet Optimize program, the Auto Threshold function lets the analyst select a baseline region for noise measurement. In a representative 0.5 min section, an equilibrated system in good working order should be able to deliver a noise reading less than 5 nS peak to peak for the initial eluent concentration, and less than 10 nS peak to peak for the higher eluent concentration.

Method detection limits were established for six anions using both deionized water and 8 mg/L morpholine and are summarized in Table 3. Calibration curves were obtained with standards prepared in deionized water and in 8 mg/L morpholine using the concentrations listed in Table 4.

Table 3. 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	0.018	0.025
Chloride	0.044	0.12
Nitrate	0.55	0.59
Phosphate	0.66	0.76
Sulfate	0.11	0.17
Oxalate	0.21	0.54

[a]8 mg/L morpholine

[b]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.

Anion	Level 1	Level 2	Level 3	Level 4
Fluoride	0.1	0.3	1	3
Chloride	0.3	1	3	10
Nitrate	0.3	1	3	10
Phosphate	0.3	1	3	10
Sulfate	0.3	1	3	10
Oxalate	0.3	1	3	10

Results for the six anions of interest yielded a linear response in both matrices with coefficients of determination (r^2) greater than 0.99. Table 5 lists the r^2 values as well as the slopes and intercepts for the six 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.

Table 5. Calibration curve parameters for trace anion determination by high volume/direct injection ion chromatography.

Anion	r^2 Slope Intercept	DI Water	Morpholine-treated Water[a]
Fluoride	r^2	0.9988	0.9936
	Slope	1.02×10^{-4}	8.42×10^{-5}
	Intercept	0.047	0.317
Chloride	r^2	0.9988	0.9974
	Slope	1.75×10^{-4}	1.67×10^{-4}
	Intercept	0.311	0.112
Nitrate	r^2	0.9919	0.9936
	Slope	5.25×10^{-4}	5.70×10^{-4}
	Intercept	0.550	0.294
Phosphate	r^2	0.9954	0.9975
	Slope	5.65×10^{-4}	5.60×10^{-4}
	Intercept	0.455	0.295
Sulfate	r^2	0.9997	0.9998
	Slope	2.74×10^{-4}	2.72×10^{-4}
	Intercept	-0.0762 -	0.300
Oxalate	r^2	0.9969	0.9955
	Slope	2.76×10^{-4}	2.68×10^{-4}
	Intercept	0.0145	-0.400

[a]8 mg/L morpholine

Correctly timing the point at which the gradient steps to the higher eluent concentration is important, as variations in the eluent composition can alter the selectivity of the method. It is therefore necessary to prepare the eluent in a consistent fashion to ensure reproducible chromatography. Nitrate elutes on the upward slope of the chromatogram, complicating integration. However, by using "Start Peak Detection" and "Stop Peak Detection" commands in PeakNet, it is possible to reproducibly integrate this peak. This set of commands is also helpful to place before and after the points where carbonate is expected to elute, thus avoiding integration of carbonate.

Precautions

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, microorganisms, 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.

When conducting analyses at trace levels, the sources of contamination are numerous. Wear disposable gloves (for clean room electronics applications) when handling apparatus that makes contact with eluent, standard, or samples. Rinse the gloves with deionized water after putting them on and then air dry. Do not dry with paper towels. 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 (eluent containers, injector, pump, valves, tubing, columns, suppressor, and conductivity cell) are all potential sources of contamination. Take care when switching from a system setup that had previously come in contact with significant concentrations of anions. Rinse with high-purity water to reduce residual contamination.

Conclusion

Use of an eluent step change program with a 2 mm Dionex IonPac AS14 column enables a fast separation of common anions. It is possible to achieve sub-µg/L detection limits for anions in high-purity water by direct injection in less than 15 minutes. 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 deionized water and power plant treated waters.

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