DIONEX

Application Note 85

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Determination of Trace Anions in Organic Solvents

INTRODUCTION

In the manufacture of semiconductor materials, a great deal of attention is focused on minimizing sources of contamination. Yield and reliability can be significantly compromised by ionic contamination. Of particular interest are those chemicals that come into contact with micro-electronic circuitry, such as isopropyl alcohol, acetone, and *N*-methyl-2-pyrrolidone.

Analysis of trace anions in solvents by wet chemical methods is laborious and time consuming. Procedures involve evaporation of a large volume of sample for several hours on a hot plate.[1] Anions are determined by either colorimetric or turbidimetric methods, and each anion must be determined separately.

This Application Note describes a method for determining trace anions in water-miscible organic solvents by ion chromatography. Anions are removed from the solvent matrix and concentrated on a 4-mm IonPac® AG9-HC column. These concentrated anions are then eluted to a 2-mm IonPac AS9-HC analytical column set, where separation occurs. Method detection limits (MDLs) for chloride, sulfate, phosphate, and nitrate are less than 1 µg/L. The procedure is automated and yields an analysis for the four anions in less than 45 min. This method is an improvement over a method previously reported using a 4-mm AS10 column because it yields lower method detection limits and can be applied to a variety of organic solvents.[2]

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:

- GP50 Gradient Pump, microbore configuration
- CD20 Conductivity Detector with a temperature controlled conductivity cell (DS3)
- LC20 Chromatography Enclosure, PEEK, with a second channel kit/two Rheodyne valves, rear-loading

Dionex DXP Single Piston Pump

AC2 Power Control Accessory (P/N 46057) to control DXP pump and CAM

Controlled Air Module (CAM-1) (P/N 38730) to actuate loading valve

Low Pressure 3-Way Valve, 10-32 fittings (P/N 45009) (loading valve)

Pressurizable Reservoir Chamber (P/N 37053)

4-L Plastic bottle assemblies, two for external water mode (P/N 39164)

PeakNet Chromatography Workstation

40 ft (1219 cm) of 0.030-in. (0.75-mm) i.d. PEEK tubing (P/N 44777) to construct a 5-mL loop

High-density polyethylene bottles as sample containers

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)

0.5 M Dionex Sodium Carbonate Eluent Concentrate (P/N 37162)

Sodium and Potassium salts, ACS reagent grade, for preparing anion standards (Fisher Scientific; see Table 2) or 1000-ppm anion standards

CONDITIONS

Columns:	IonPac AG9-HC Guard (2 mm) IonPac AS9-HC Analytical (2 mm) IonPac AG9-HC Concentrator (4 mm) ATC-1 Anion Trap Column (4 mm)
Eluent:	8.0 mM Sodium carbonate/ 1.5 mM Sodium hydroxide
Eluent Flow Rate:	0.25 mL/min
Rinsing Flow Rate:	2.0 mL/min
Sample Volume:	5.0 mL
Detection:	Suppressed conductivity, ASRS®-ULTRA, AutoSuppression® external water mode
Current Setting:	100 mA
Expected System Backpressure:	13.1 MPa (1900 psi)
Expected Background Conductivity:	21 µS
Pump Program:	See Table 1 below

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent Solution

8.0 mM Sodium carbonate/1.5 mM Sodium hydroxide

Add 16 mL of 0.5 M sodium carbonate and 0.12 g of 50% sodium hydroxide directly to 900 mL of deionized water in a 1-L volumetric flask. Dilute to a final volume of 1000 mL. Transfer this solution to an eluent container and vacuum degas for 5 min.

Deionized Water for Rinsing

Vacuum degas 1 L of deionized water in a clean, 1.0-L eluent bottle while sonicating for 15 min. To prevent contamination of the sample with anionic impurities in the rinse solution, an anion trap column (ATC-1) is used. This column contains a high-capacity, anion-exchange resin in the hydroxide form. The ATC-1 is prepared for use by flushing the column separately and off-line with 200 mL of 200 mM sodium hydroxide followed by 100 mL of deionized water at 2 mL/min.

Standard Solutions

Stock Anion Standard Solution (1000 mg/L)

Use commercially available 1000 ppm anion standards or prepare 1000-mg/L standards of each ion by dissolving the corresponding mass of the salt in 1000 mL of deionized water (see Table 2). The salts should be dried at 105 °C for 30 min prior to weighing.

Table 2 Masses of Salts for 1000 mg/L Ion Standards

Anion	Salt	Weight (g)
Chloride (Cl^-)	Sodium chloride (NaCl)	1.648
Sulfate (SO_4^{2-})	Potassium sulfate (K_2SO_4)	1.814
Phosphate (HPO_4^{2-})	Potassium phosphate, monobasic (KH_2PO_4)	1.418
Nitrate (NO_3^-)	Sodium nitrate ($NaNO_3$)	1.371

Working Standard Solution (1 mg/L)

To prepare a mixed working standard solution, combine 1 mL of each anion stock solution with deionized water and dilute to a final volume of 1000 mL.

Table 1 Pump Program

Time (min)	E1 (%)	Inject	Column	Relay 1 (Pump)	Relay 2 (Sample Valve)	Figure	Remarks
Initial	100	0	0	0	0	1	Conc. column in-line, fill sample loop
0.00	100	0	1	0	0	2	Conc. column off-line
0.10	100	0	1	1	0	2	DXP Pump on
4.90	100	0	1	0	0	2	DXP Pump off
5.00	100	1	0	0	1	3	Inject, loop in load position
35.00	100	1	0	0	1	3	
35.01	100	0	0	0	1	3	

Calibration Standards

Prepare at least three different calibration standards at different dilutions of the working standard. Select a range similar to the expected concentrations in the samples. The organic solvent and the amount of carbonate present in the sample can affect the response and retention time for the analytes of interest. The method of standard addition (adding one or more increments of a standard solution to sample aliquots of the same size) can be used to account for the matrix effect of the unknown sample.[3]

SAMPLE LOADING

Construct a 5-mL sample loop with a 432-in. (1097-cm) piece of 0.03-in. (0.75-mm) i.d. PEEK tubing. Samples of an organic solvent can be directly injected into the sample loop without dilution. An autosampler such as the Dionex AS40 can be used for automated loading of the sample loop in cases where detection limit requirements are above 100 µg/L (ppb). When lower limits are required, a pressurized reagent reservoir is a better choice for loading. This technique uses gas pressure to push sample from a sample container into the sample loop.[4]

PROCEDURE

The determination of trace anions in water-miscible solvents is accomplished using an 8.0 mM sodium carbonate/1.5 mM sodium hydroxide eluent with the IonPac AS9-HC. The solvent sample is directly loaded onto a 4-mm AG9-HC without dilution. The solvent matrix is eliminated by washing the AG9-HC with deionized water, while the anions of interest are retained. This method takes advantage of the solvent compatibility of the column. Anion concentrations in the solvent are quantified by using calibration plots based on standards prepared in water or by standard addition. Trace anion analysis of solvents is accomplished in four steps: (1) filling the sample loop, (2) loading the concentrator, (3) eliminating the solvent matrix, and (4) eluting the retained ions. Figures 1–3 illustrate how the system performs these tasks.

First, the sample is loaded into the 5-mL sample loop. A pressure of approximately 54 kPa (8 psi) applied to the sample reservoir ensures that the sample loop is consistently filled without bubbles (Figure 1). To ensure that the loop contents contain a representative sample, at least four loop volumes (4 x 5 mL = 20 mL) should be passed through the sample loop.[5] After the sample loop has been filled, deionized water pushes the sample out of the loop and onto the concentrator column in the direction opposite the eluent flow (Figure 2). Anions are retained on the concentrator column and the solvent matrix is eliminated by washing the IonPac AG9-HC concentrator column with deionized water at 2 mL/min. This step takes 5 min and uses 10 mL of deionized water. Finally, by activating the "column" valve on the GP50, the concentrator column is switched in-line with the eluent stream and the analytical columns (Figure 3). The anions are eluted from the concentrator column and separated on the analytical column.

DISCUSSION AND RESULTS

The microbore format was chosen for the analytical columns and suppressor because it has several advantages.[6] There is a fourfold increase in mass sensitivity for the microbore (2 mm) over the standard bore (4 mm) format with no loss in concentration sensitivity. Thus, smaller amounts of sample are required. This facilitates convenient and faster loop loading. The microbore format also offers low eluent consumption and less eluent waste.

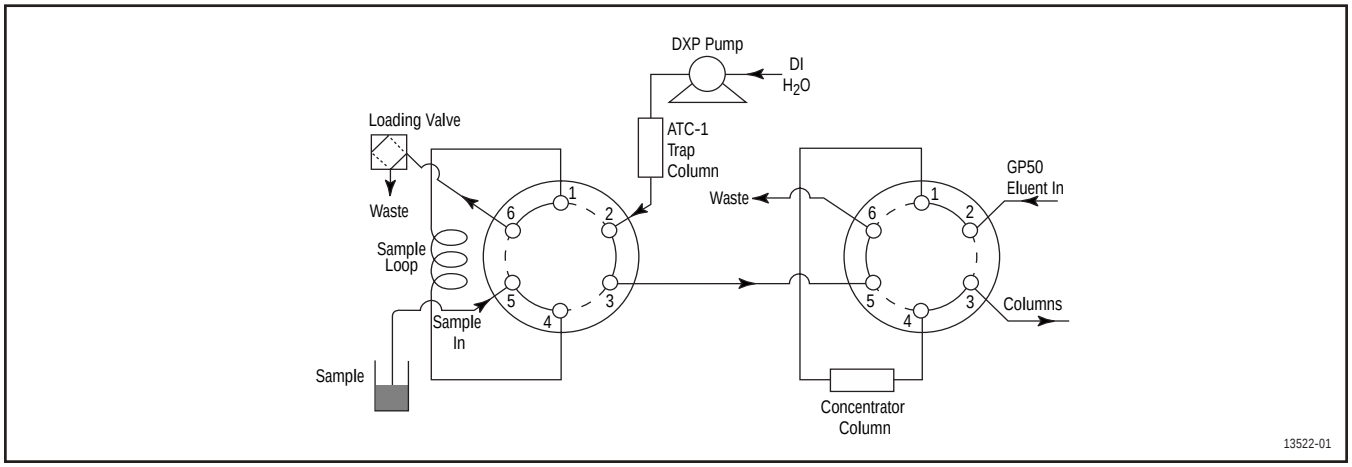

***Figure 1**. Loading the sample loop.*

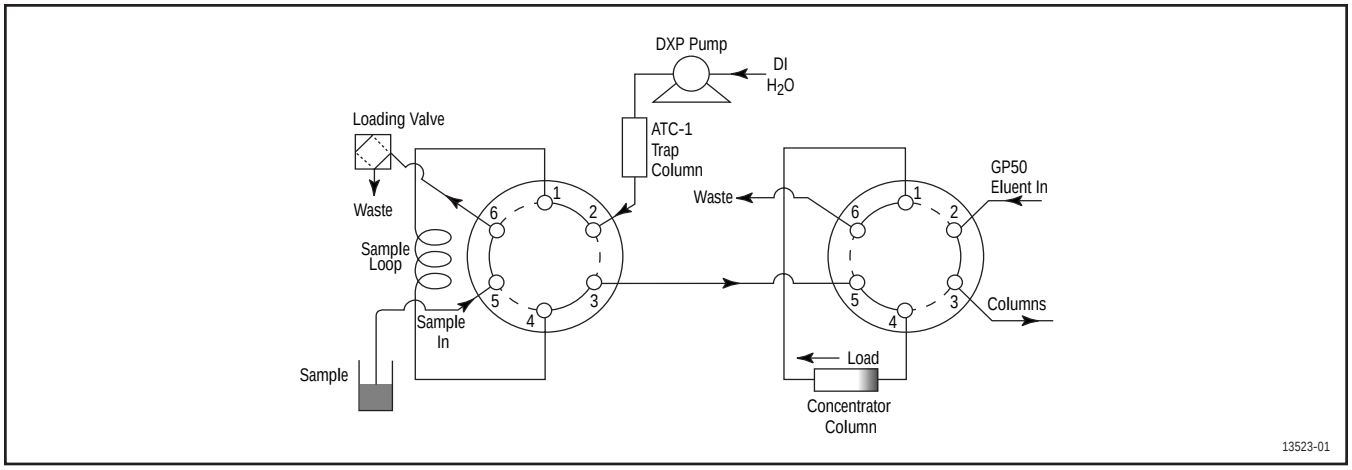

***Figure 2**. Loading the concentrator column and eliminating the matrix.*

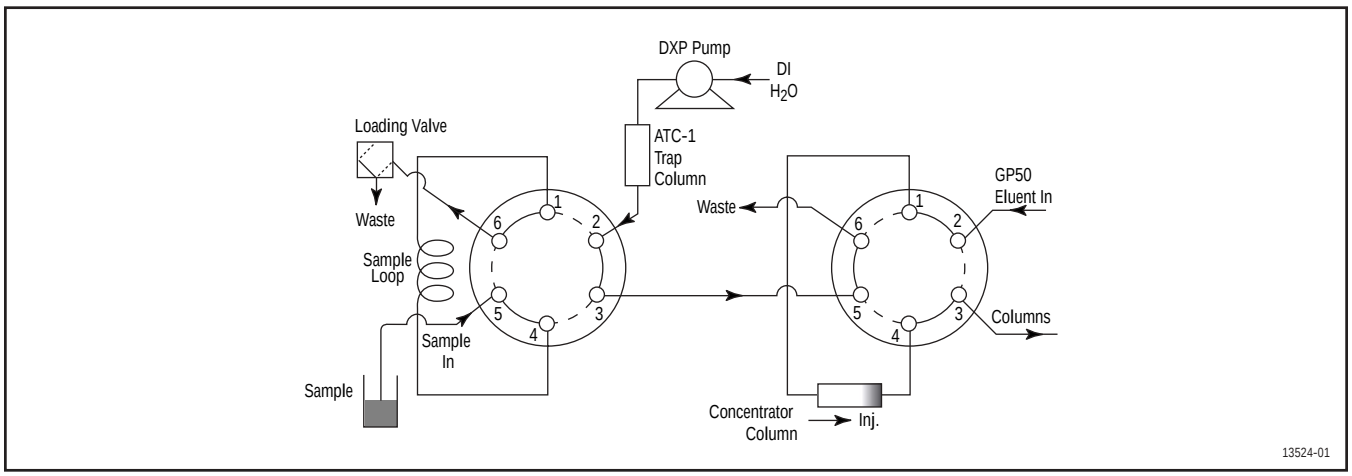

***Figure 3**. Chromatography of the retained ions.*

Representative chromatograms of semiconductor-grade isopropyl alcohol "as received" and spiked with the four anions of interest are shown in Figures 4 and 5, respectively. A summary of the recovery data for isopropyl alcohol is shown in Table 3. The concentrations are corrected by subtracting the amount of the analytes of interest found in the deionized water blank.

A system blank is determined by using deionized water as the sample. The blank establishes baseline anion concentrations from such sources as the polyethylene sample container and the deionized water. Figure 6 shows a representative blank; none of the anions of interest were detected in the blank. A calibration standard prepared in water is shown in Figure 7. Fluoride quantification is hampered because it elutes in the system void.

This method was also evaluated with other high-purity, water-miscible organic solvents. Representative chromatograms for acetone and *N*-methylpyrrolidone are shown in Figures 8 and 9, respectively. A shift in retention time was observed for some of the later-eluting anions in these solvents. A summary of the MDLs and Semiconductor Equipment and Materials International (SEMI) guidelines

Table 3 Spike/Recovery of Trace Anions in 99% Isopropanol

Anion	IPA Blank Concentration (µg/L ± S.D., n=5)	Spike in IPA (µg/L)	(Found) - (Avg. Blank) (µg/L ± S.D., n=5)	Recovery (%)
Chloride	0.574 ± 0.030	5.0	5.01 ± 0.049	100
	0.546 ± 0.029	5.0	4.39 ± 0.27	88
Nitrate	0.551 ± 0.130	5.0	5.62 ± 0.29	112
	0.372 ± 0.063	5.0	5.11 ± 0.55	102
Sulfate	0.123 ± 0.012	5.0	4.91 ± 0.40	98
	0.145 ± 0.024	5.0	4.17 ± 0.35	83
Phosphate	<MDL	5.0	4.74 ± 0.32	95
	<MDL	5.0	4.28 ± 0.33	84

< MDL = Less than Method Detection Limit

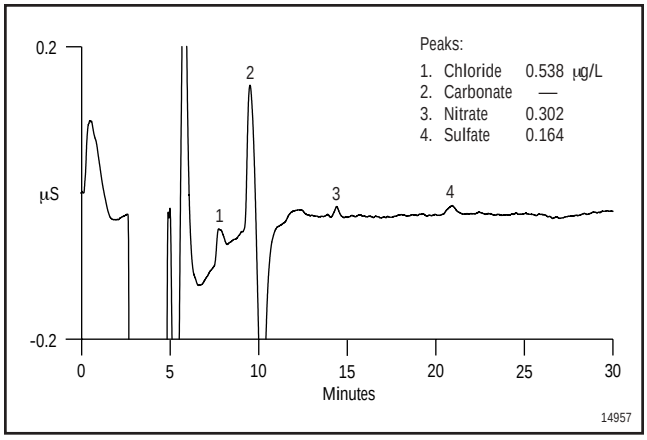

***Figure 4**. Unspiked 100% isopropanol.*

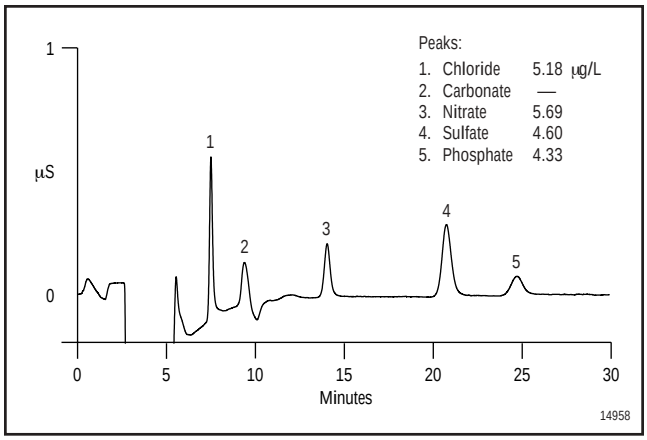

***Figure 5**. Spiked isopropanol (99% isopropanol and 1% aqueous standard).*

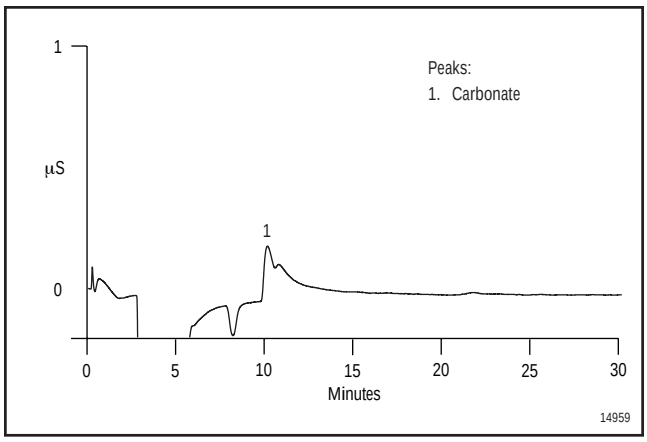

***Figure 6**. Representative system blank.*

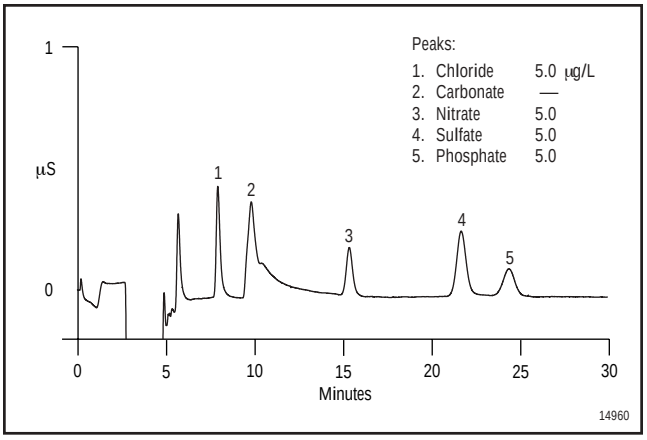

***Figure 7**. Analysis of aqueous standard using the IC with matrix elimination procedure.*

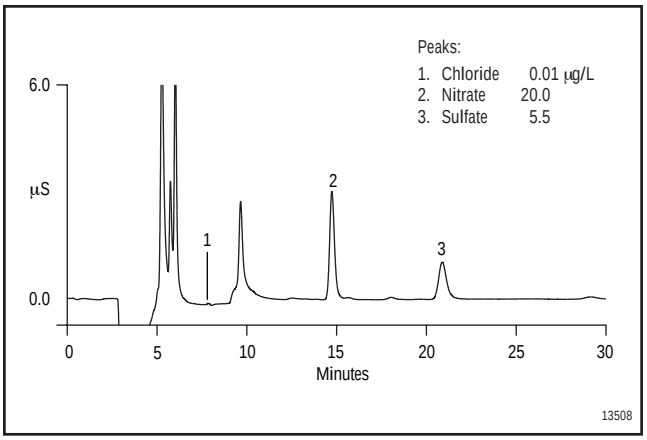

***Figure 8**. Trace anion determination of semiconductor-grade acetone.*

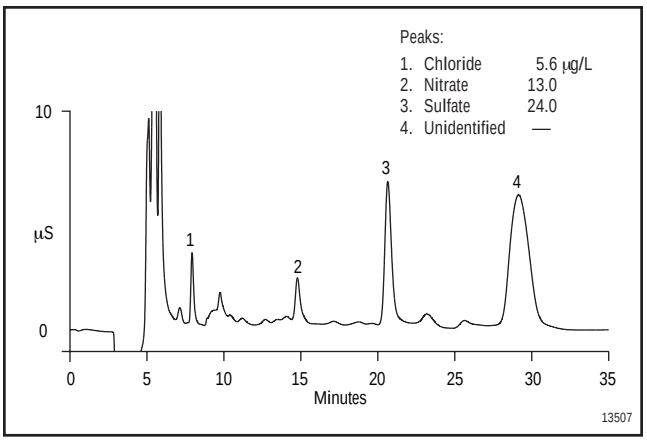

***Figure 9**. Trace anion determination of semiconductor-grade* N*-methylpyrrolidone.*

Table 4 Method Detection Limits and SEMI Specifications				
Anion	**Method Detection Limit[a] (μg/L)**	**IPA SEMI[b] Spec. C8.7-92 (μg/L)**	**Acetone SEMI[b] Spec. C1.2-96 (μg/L)**	**NMP SEMI[b] Spec. C8.9-94 (μg/L)**
Chloride	0.592	50	200	300
Sulfate	0.758	50	—	250
Phosphate	0.754	50	100	250
Nitrate	0.647	50	—	400

[a] Method Detection Limit (MDL) based on ordinary least-squares regression analysis in isopropyl alcohol matrix[8]

[b] SEMI = Semiconductor Equipment and Materials International.[7]

for maximum levels in isopropanol, acetone, and *N*-methylpyrrolidone are presented in Table 4.[7] MDLs were calculated using an ordinary least-squares regression analysis of the calibration data in the IPA matrix.[8] To determine linearity of response for the analytes of interest, aqueous standards were spiked into 99% isopropyl alcohol. Each of the four anions had a linear response with r^2 values greater than 0.99 from 1 to 10 μg/L.

CONCLUSION

Combined use of a 4-mm IonPac AG9-HC concentrator column and matrix elimination provides an improved analysis of anions in water-miscible organic solvents. Chloride, sulfate, phosphate, and nitrate are determined to sub-μg/L levels with acceptable recovery. This technique can be very useful as a quality control test in many semiconductor applications. This method is applicable to water-miscible solvents that are compatible with the polymeric pathway in the IC instrumentation. Solvents that have been successfully used with this method include: isopropyl alcohol, acetone, *N*-methylpyrrolidone, acetonitrile, and methanol.

PRECAUTIONS

When performing trace analysis, special care must be taken to minimize contamination. It is very important to use only the highest quality deionized water. Any ionic contamination present in the deionized water will be magnified in proportion to the volume needed for the rinsing step. To ensure the quality of the rinse water, the ATC-1 is periodically regenerated with the procedure described in the "Preparation of Solutions and Reagents" section. The AS9-HC should only be used in a pH range between 0 and 12. Success of this method is dependent on maintaining a consistent flow rate for the DXP sample loading pump.

A polyethylene container should be soaked for at least 24 hours with 18 MΩ-cm deionized water and rinsed several times prior to use. (Use of a glass container results in low recovery of phosphate.) This container is then placed in the pressurized sample reservoir. Disposable gloves (for cleanroom electronics applications) should be worn at all times when handling apparatus that contacts standard or sample. All containers should be dedicated for trace analysis and copiously rinsed with 18 MΩ-cm deionized water before use.

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LIST OF SUPPLIERS

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