Determination of trace anions in organic solvents using matrix elimination and preconcentration

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Introduction

Anion contamination introduced during manufacturing processes can ruin semiconductors and computer components. Trace contaminants in solvents used during manufacturing can cause short circuits, defects in deposition, and corrosion. Component defects such as these reduce yields, which increases manufacturing costs and waste. As device geometries shrink, even lower levels of contamination become problematic. The computer and semiconductor industries need analytical methods to determine trace anions in solvents to help them identify contamination at different stages of manufacturing, so they can take action to prevent future contamination.

Previously, trace concentrations of anions at µg/L levels in solvents have been determined by matrix elimination using a Thermo Scientific™ Dionex™ DXP pump and pre-concentration on a Thermo Scientific™ Dionex™ IonPac™ AS9-HC 4 mm concentrator column, as described in Thermo Scientific Application Note 85[1] (AN85). The 5 mL sample required for this method is introduced to the sample loop by pneumatic feed, which allows only manual injections. The concentrated anions are separated on a Dionex IonPac AS9-HC 2 mm guard and analytical column set using manually prepared sodium carbonate and sodium hydroxide eluent. Manual eluent preparation makes

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consistency difficult and the carbonate concentration in the sodium hydroxide solution used to prepare the eluent varies due to atmospheric CO_2.

This update to AN85 describes an automated method that improves consistency and lowers detection limits, using the Thermo Scientific™ Dionex™ ICS-3000 DP Dual Pump, EG Eluent Generator, and DC Detector/ Chromatography modules with updated suppressor, trap, concentrator, and analytical column technology. A Thermo Scientific™ Dionex™ AS-HV High-Volume Autosampler is used in place of the pneumatic pump to load a 2 mL solvent sample, allowing automation and freeing operator time. A potassium hydroxide eluent is electrolytically generated using a Thermo Scientific™ Dionex™ Reagent-Free™ Ion Chromatography (RFIC™) system, which supplies consistent eluent concentrations and saves operators the time and labor of eluent preparation. Signal response is also increased because the background of the KOH eluent can be suppressed to a much lower level than that of the carbonate eluent.

This method successfully determines trace anions from high ng/L to low µg/L concentrations in isopropyl alcohol, methanol, acetone, and n-methyl-2-pyrrolidone, with improved method detection limits, from a 60% smaller sample injection. The method easily meets the Semiconductor Equipment and Materials International (SEMI®) specifications for solvents, with typically 100- to 2,800-fold lower method detection limits (MDLs) than the SEMI specifications require.

Experimental
Equipment
- Dionex ICS-3000 RFIC system* consisting of:

  – DC Detector/Chromatography module with dual temperature zones, two injection valves, and one CD Conductivity Detector and integrated cell (P/N 079829)

  – DP Dual Pump module with degas module

  – EG Eluent Generator module with Thermo Scientific™ Dionex™ EluGen™ EGC II KOH cartridge Replaced by Dionex EGC 500 KOH cartridge (P/N 075778), Thermo Scientific™ Dionex™ Continuously Regenerated Anion Trap Column (CR-ATC 600, P/N 088662) P/N 074532), and Thermo Scientific™ Dionex™ Continuously Regenerated Anion Trap Column (CR-ATC, P/N 060477)

  – Dionex AS-HV High Volume Autosampler with internal peristaltic pump (P/N 064508), PEEK™ needle (P/N 064254), and 15-position sample rack (P/N 064234) for 250 mL Thermo Scientific™ Nalgene™ poly bottles

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

- Replaced by Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) 7.2 version 10 for system control and data handling

- Tubing:

  – 30 ft or 900 cm of green PEEK (0.76 mm or 0.03 in i.d., P/N 44777 per inch) for eluent waste lines (two 120 cm lengths), 2 mL sample loop (450 cm), and Dionex AS-HV Autosampler sample line (185 cm)

  – 1 ft or 30 cm of red PEEK (0.13 mm or 0.005 in i.d., P/N 052310 for 5 ft) for eluent lines after Inj. Valve 1 on System 1

  – 3 ft or 91 cm of black PEEK (0.25 mm or 0.01 in i.d., P/N 052306 for 5 ft) for liquid line connections for both systems

  – Backpressure loop for 2 mm suppressor (P/N 45878) or 1 ft of black PEEK (0.25 mm)

  – 2.5 ft or 76 cm of yellow PEEK (0.08 mm or 0.003 in i.d., P/N 052301 for 5 ft) for system backpressure loops

  – Santoprene® (Exxon Mobile Corp.), 1 extra (2.06 mm or 0.08 in i.d., Dionex P/N 064521) for the sample loading line on internal peristaltic pump

  – Low pressure Teflon® (The Chemours Co.) tubing (1.6 mm or 0.063 in i.d., P/N 014157) for the Thermo Scientific™ Dionex™ Carbonate Removal Device (CRD 200), eluent containers, and Dionex AS-HV reservoir container liquid lines, and Thermo Scientific™ Dionex™ ASRS™ ULTRA II suppressor regenerant and degas waste lines

- One 4 L water container for Dionex AS-HV Autosampler rinse fluid reservoir (P/N 063292)

- Four to six additional 2 L eluent bottles (P/N 062510) (one bottle for Pump 1 eluent; two bottles for Pump 2 matrix elimination if water is replaced daily, four to run the system continuously over a weekend; and one bottle for the conditioning solution)

- 250 mL Nalgene poly bottles with caps and septa (package of 72, P/N 064232) for the Dionex AS-HV Autosampler

Reagents and standards

Use only ACS reagent grade chemicals for all reagents and standards.

- Deionized water, Type 1 reagent-grade, 18.2 MΩ·cm resistivity or better

- Thermo Scientific™ Dionex™ Chloride Standard, 1,000 mg/L, NIST Traceable (P/N 037159)

- Thermo Scientific™ Dionex™ Combined Five Anion Standard, NIST Traceable (P/N 037157)

- Potassium phosphate, monobasic (MilliporeSigma, P/N PX1565-1)

- Sodium chloride, crystalline (JT Baker® Ultrapure Bioreagent, P/N 4058-01)

- Sodium nitrate, crystalline (Fisher Scientific™, P/N S343-500)

- Sodium sulfate, granular (MilliporeSigma, P/N SX0760-1)

- Thermo Scientific™ Dionex™ Sulfate Standard, 1,000 mg/L, NIST Traceable (P/N 037160)

Samples

- Class 10 Semiconductor grade solvents: isopropyl alcohol, N-methyl-2-pyrrolidone (NMP), acetone, and methanol.

Conditions

Sample preparation: System 2

Trap Column:	Thermo Scientific™ Dionex™ IonPac ATC-HC, 9 × 75 mm(P/N 059604)
Pump 2 Flow Rate:	2.0 mL/min
Carrier:	Degassed deionized water
Matrix Elimination:	10 mL[a]
Peristaltic Pump Flow Rate:	1.2 mL/min (AS-HV)
Inj. Volume:	2 mL
Sample Load Volume:	5 mL (Enter in Sequence)
Rinse Volume:	7 mL (Flush)

AS-HV Sample Load Mode:	Pull
Typical System Backpressure:	~900 psi
Prep. Time with Overlap:	11 min
Prep. Time without Overlap:	17 min

[a]20 mL when determining anions in NMP mg/L stock standards.

Conditions

Analytical: System 1

Columns:	Thermo Scientific™ Dionex™ IonPac AG18 guard, 2 × 50 mm (P/N 060555) Dionex IonPac AS18 analytical, 2 × 250 mm (P/N 060553)
Flow Rate:	0.25 mL/min
Eluent:	22 mM KOH from -2 to 15 min, 22 to 48 mM KOH from 15 to 25 min, 65 mM KOH from 35 to 40 min
Eluent Source:	EGC II KOH
Column Temp.:	30 ºC
Concentrator:	Thermo Scientific™ Dionex™ IonPac UTAC-ULP1, 5 × 23 mm (P/N 063475)
Detection:	Suppressed Conductivity, Dionex ASRS ULTRA II Anion Self-Regenerating Suppressor 2 mm, recycle mode-Replaced by Thermo Scientific™ Dionex™ ADRS™ 600 (2 mm), P/N 088667), 41 mA)
Carbonate Removal:	Dionex CRD 200 device, 2 mm (P/N 062986) installed between the suppressor and the detector
Typical Background:	<2 µS
Typical System Backpressure:	~2200 psi
Typical Noise:	<3 nS
Run Time:	33 min
Total Analysis Time:	44–50 min

Preparation of solutions and reagents

It is essential to use high quality, Type 1 water, >18.2 MΩ·cm, that contains as little dissolved carbon dioxide as possible.

Preparation of rinse fluid reservoir for the Dionex AS-HV Autosampler

Start preparing the 4 L rinse fluid reservoir for the Dionex AS-HV Autosampler two or more days prior to use. Rinse the inside of the container five times with Type 1 deionized water, fill it to just below the fittings, cap the container, and let it soak for two days. Discard the soaking water and fill the container with fresh Type 1 deionized water to just below the fittings. Connect the bottle to the rinse fluid reservoir tubing on the peristaltic pump (Figure 1). As this bottle is open to the air, the deionized water should be replaced daily if possible.
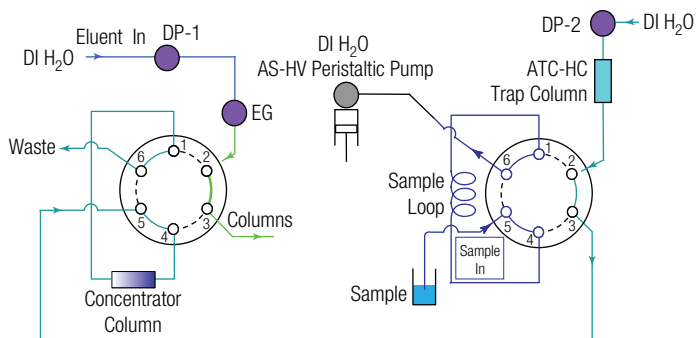

Figure 1. Matrix elimination configuration using the Dionex AS-HV High-Volume Autosampler and the Dionex ICS-3000 DP Dual Pump module, D/C Detector/Chromatography module dual valves, and Dionex EG Eluent Generator

Preparation of eluent (degassed deionized water)

To run analyses unattended over the weekend, five 2 L eluent bottles are required (one for Pump 1 and four for Pump 2). If eluent is added daily, only two 2 L bottles are needed for Pump 2. To link the eluent bottles, connect the bottles in series with the first bottle pressurized by the inert gas and the last bottle connected to Pump 2, Eluent A line. Prepare the 2 L eluent bottles two or more days prior to use, as described in the Preparation of Rinse Fluid Reservoir for the Dionex AS-HV Autosampler section. To prepare the eluent for Pump 1, degas 2 L of Type 1 deionized water using ultrasonic agitation and applied vacuum to aid in removing the gas bubbles. Pour the degassed deionized water into a 2 L pre-cleaned

eluent bottle. Connect the eluent bottle to the Eluent A line from Pump 1, place the eluent bottle under 4–5 psi of helium or other inert gas, and prime Pump 1 with the new eluent. Prepare degassed deionized Type 1 water for Pump 2 in the same way.

Preparation of 200 mM sodium hydroxide conditioning solution

To condition the Dionex IonPac ATC-HC trap column, prepare 200 mM sodium hydroxide conditioning solution. Clean a 10 mL graduated transfer pipette with deionized water by filling it and dispensing it three times. Expel the excess liquid in the bottom of the pipette and fill the pipette with 50% sodium hydroxide solution (Fisher Scientific) from the center of the reagent bottle. Transfer 16 g of the solution into an eluent bottle, then dilute to 1,000 g total with degassed deionized water. Cap the eluent bottle and swirl gently to mix. Connect the eluent bottle to Pump 1 Eluent B line, and place under ~4–5 psi of helium or other inert gas. Do not use sodium hydroxide pellets to prepare the eluent as the pellets are coated with sodium carbonate. Sodium hydroxide eluent preparation is thoroughly discussed in Technical Note 71.[2]

Preparation of stock standards

Individual 1,000 mg/L stock standards can be prepared from the solid compound or acquired commercially as certified reagents. To prepare individual stock solutions of 1,000 mg/L chloride, sulfate, nitrate, and phosphate, weigh the amount of reagent grade compound (Table 1) into a 125 mL HDPP sample bottle and dilute with deionized water to 100.00 g total weight. Shake each stock solution to fully dissolve the compound.

Table 1. Amount of compound used to prepare 100 mL of 1,000 mg/L individual stock solutions

Anion	Compound	Mass (g)
Chloride	Sodium chloride (NaCl)	0.165
Sulfate	Sodium sulfate (Na_2SO_4)	0.148
Nitrate	Sodium nitrate ($NaNO_3$)	0.137
Phosphate	Potassium phosphate, monobasic (KH_2PO_4)	0.143

Preparation of intermediate and working standards

To prepare a combined 1,000 µg/L intermediate standard from chloride, nitrate, sulfate, and phosphate stock solutions in water, pipette 100 µL each of the 1,000 mg/L individual stock solutions into a 120 mL polypropylene bottle. Dilute with deionized water to 100.00 g total weight. Alternatively, pipette 1,000 µL of the Dionex Combined Five Anion Standard into a 120 mL polypropylene bottle. Dilute with deionized water to 100.00 g total weight. This will generate an intermediate standard containing 200 µg/L fluoride, 300 µg/L chloride, 1,000 µg/L nitrate, and 1,500 µg/L each of sulfate and phosphate. Follow directions below for preparation of the working standards and recalculate the final concentrations accordingly.

Prepare the Nalgene 250 mL polypropylene autosampler bottles for the solvents and µg/L standards two days or more prior to the standard or sample preparation. Rinse each bottle five times with deionized water, fill it to the top with deionized water, cap it, and let it soak overnight. Repeat this daily until bottles are needed for the µg/L standards. See Application Update 142[3] for additional precautions needed for determinations of µg/L anion concentrations.

To prepare working standards 1–9 in water (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, and 50 µg/L chloride, nitrate, sulfate and phosphate), pipette 10, 20, 50, 100, 200, 500, 1,000, 2,000, and 5,000 µL of the combined 1,000 µg/L intermediate standard into nine separate 250 mL polypropylene bottles. Dilute these working standards with degassed deionized water to 100.00 g total weight and mix thoroughly. Prepare low-µg/L standards daily, and mg/L standards monthly.

Preparation of samples

Class 10 solvent samples can be analyzed directly without any preparation. For solvents that have high evaporation rates, insert a 3 × 3 cm square piece of aluminum foil under the pre-split septa and carefully tighten the cap. Replace the pierced foil with a fresh piece immediately after the sample has been injected. The foil seals the sample bottle and reduces the amount lost from evaporation. Determine anions in these samples immediately.

To prepare 2 µg/L and 10 µg/L spike recovery samples of individual solvents, weigh 99 g of the solvent into two separate 250 mL polypropylene bottles. Pipette 200 and 1,000 µL, respectively, of the 1,000 µg/L intermediate standard and 800 and 0 µL, respectively, of degassed deionized water into the bottles. Swirl to mix. Cap immediately.

System preparation and setup

This application uses both systems to determine anions in solvents. System 2 loads the sample and transfers it to the concentrator on System 1. System 1 flushes the water-miscible solvent from the concentrator column, elutes the retained anions onto the analytical column, separates them, and detects them using suppressed conductivity. The setups for the individual modules, components, and system are thoroughly described in the operator's and installation manuals[4,5] for the Dionex ICS-3000 chromatography system, and in the Chromeleon Help menus.

Sample preparation system setup (System 2)

To set up the sample preparation system (System 2), install the Dionex IonPac ATC-HC trap column, a 1,000 psi backpressure loop, and a 2 mL sample loop. Install the Dionex IonPac ATC-HC trap column on Pump 2 with black PEEK (0.01 in. or 0.25 mm i.d.) tubing. Condition the trap column with 200 mM sodium hydroxide conditioning solution and deionized water according to the product manual.[6] Install a backpressure loop rated at 1,000 psi at 2 mL/min [~6-in. or 15-cm yellow PEEK (0.003 in. or 0.08 mm i.d.) tubing] from the trap column to Port P on Inj. Valve 2. To prepare a 2 mL sample loop, cut a 440 cm section of green PEEK (0.03 in. or 0.76 mm i.d.) tubing. Determine the sample volume by the difference in weight between the sample loop filled with deionized water and empty. Install the sample loop in Ports L (1, 4) in Inj. Valve 2. Install a ~6-in. (~15-cm) length of black PEEK (0.25 mm or 0.01 in. i.d.) tubing from Port C on Inj. Valve 2 to Port S on Inj. Valve 1 to connect the sample loop to the concentrator (Figure 1). Do not overtighten any of the fittings on Valve 2 as this can cause restrictions in the liquid flow and prevent sample loading by the Dionex AS-HV Autosampler.

Analytical system setup (System 1)

To set up the analytical system (System 1), condition and install the Dionex ASRS ULTRA II suppressor, Dionex Carbonate Removal Device CRD 200, Dionex EluGen EGC II KOH cartridge, and Dionex CR-ATC Continuously Regenerated Anion Trap Column according to the installation instructions in the product manuals[7,8] and the Dionex ICS-3000 operator's manual.[5] Use black PEEK tubing for the liquid connections before Inj. Valve 1 and red PEEK tubing after Inj. Valve 1. Install the suppressor with the 2 mm backpressure loop. Measure the system backpressure directly from the pump to the cell inlet with and without the 2 mm backpressure tubing in the cell outlet. Adjust the length of the backpressure loop until the difference in backpressure is 30–40 psi. Do not allow the backpressure to exceed 100 psi. A system backpressure of >100 psi can irreversibly damage the Dionex CRD 200 device and the Dionex ASRS ULTRA II suppressor.

To install the Dionex IonPac AS18 column set and the Dionex UTAC concentrator column, refer to the product manuals.[9,10] Install the Dionex IonPac AS18 column set into Port C of Inj. Valve 1. Install the Dionex IonPac UTAC-ULP1 concentrator column in Ports L (1, 4) in Inj. Valve 1 with a shorter length of red PEEK tubing in Port 4 (between Port C and Port S) and a longer length of black PEEK tubing in Port 1. Install a green PEEK tubing waste line in Port W. (Port S is connected to Port C on Inj. Valve 2.) Install a ~21 in. (~54-cm) length of yellow PEEK tubing after the degas module and before Inj. Valve 1 to bring the total system backpressure to between 2,200 and 2,400 psi.

Dionex AS-HV Autosampler setup

To set up the Dionex AS-HV Autosampler, install the spill tray, rack location mat, 15-position sample rack, and fixed rinse reservoir. Connect the RS-232 cable. Set the DIP switch, and connect the peristaltic rinse and sample pump, sample loop, and tubing according to the installation guide in Appendix B of the Operator's Manual for the Dionex AS-HV Autosampler.[11] To install the spill tray, rack location mat, fixed rinse reservoir, and 15-position sample rack, follow the instructions in sections B.3.1–B.3.3, and B.3.6 in Appendix B of the operator's manual. To connect the Dionex AS-HV Autosampler to the ICS-3000 system, follow the instructions in section B.3.14 in the Appendix to connect the RS-232 cable and set the DIP.

Setting up the rinsing line of the internal peristaltic pump

The internal peristaltic pump of the Dionex AS-HV Autosampler is used in this application to rinse the PEEK sample needle and sample lines and to load the sample. The pump rotor of the peristaltic pump rotates counterclockwise, squeezing the pump's lines as it rotates, and forcing the liquid ahead of it. To connect the peristaltic pump rinsing lines to the fixed rinse and 4 L external rinse reservoirs, install the ¼ in. i.d. Nalgene waste line and the Santoprene 2.06 mm tubing according to the instructions in Appendix B.3.4 (Figure 2). Direct the free waste line to the waste container directly below the autosampler. The rinse waste solution can back up into the spill tray if the tubing is not placed properly. Install the Santoprene tubing rinse line in the outside track. (The inside track will be used for the sample loading line.) Connect the bottom end of the tubing to the inlet nipple on the fixed fluid reservoir. Connect the top end of the tubing to a pre-cleaned 4 L rinse fluid reservoir containing Type 1 deionized water, using a nipple to ¼-28 fitting, a ¼-28 union fitting, and a ¼-28 connector fitting. To minimize flow restrictions, use only the ¼-28 fitting connectors.
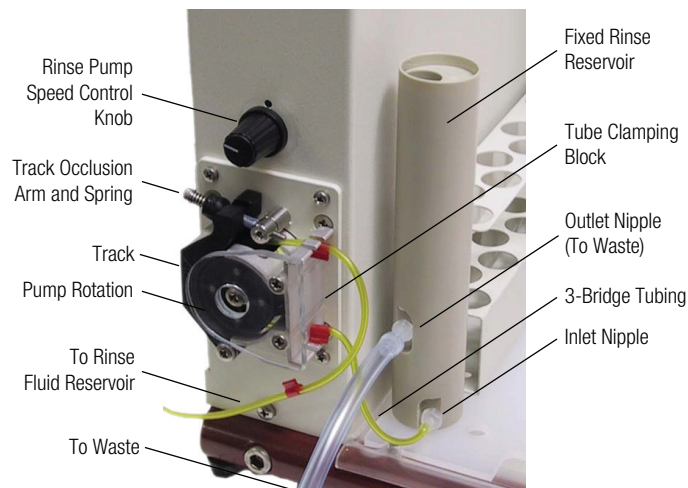

Figure 2. Tubing connections for the rinse and sample pump

Installing the sampling line

To install the sampling line in the pull mode (Figure 1), install a second piece of 2.06 mm i.d. Santoprene tubing on the inside track of the peristaltic pump rotor in the same manner as the rinsing line. Do not allow the tubing lines to fold back or restrict the flow in any way. Santoprene tubing can degrade over time and needs to be changed periodically. Connect the free end on top of the peristaltic pump to a 2 mm PTFE waste line with two connectors (nipple to ¼-28 fitting and ¼-28 to 1032 fitting connectors). It is useful to monitor the waste stream in a small container to verify that the peristaltic pump is working properly (track occlusion arm is sufficiently tight, the Santoprene tubing has not degraded, and the backpressure is not restrictive). Direct the 2 mm PTFE waste line to a container easily seen by the analyst. Do not allow the waste line to be submerged in the waste solution. Connect the bottom Santoprene tubing similarly to a ~110 cm length of green PEEK tubing. Direct the free end of the PEEK tubing to the DC and install it on Port W on Inj. Valve 2. To set the flow rate, turn the rinse speed control knob counterclockwise to ¼ turn from the right, and measure the flow rate by collecting the volume from the 2 mm PTFE waste line in a 5 mL graduated cylinder over 1 min. Adjust the rinse speed control knob until the flow rate is 1.2 mL/min. This flow rate should be confirmed periodically.

Connect a 185 cm length of green PEEK tubing from the PEEK needle under the rotating arm to the sampling arm, and to Port S of Inj. Valve 2, according to the instructions and Figures B 6–8 in Appendix B.3.8 of the AS-HV manual. The tubing must be anchored under the rotating arm with the provided tie wrap, and on two locations on the X-axis cover to prevent the sampling arm from misaligning during sampling. Create a ~24-in. (~61-cm) loop on the X-axis cover to allow for extra movement. Direct the tubing to the DC and install it on Port W of Inj. Valve 2. Before installing the tubing in Inj. Valve 2, estimate the delay volume (mL) by measuring the total length of the green tubing and multiplying that total by 0.0046 mL/cm (0.00071 mL/in.). This delay volume value is entered in the Server Configuration Setup of the Dionex AS-HV Autosampler. It is important that the sample needle is tightly secured in place and does not jerk during sample arm rotations. Adjust the PEEK sample lines and tighten the fittings on the PEEK needle until the needle is firmly secured.

Configuring the system

To configure the system for this application, connect the USB cables to the computer and modules according to the Chromeleon installation manual.[12] Power up the modules and computer and start the Chromeleon Monitor and Chromeleon Configuration programs. Create a timebase and add the modules as Dionex ICS-3000 devices. Add the DP module first and select the module address (General tab). Under the Device tab, connect Pump 1 and Pump 2 to the timebase, select *Share Waste Bottle* and *Pressure Signals*. Add the DC module and select the module serial number (General tab). Select *Inj. Valve 1* and Inj. *Valve 2* (High Pressure Valve tab), and assign control of the valves to the DC and AS, respectively (double click and select the DC or the AS on the pull down menu). Deselect any low pressure valves (Low Pressure Valve tab) and any other high pressure valves (High Pressure Valve tab). Add the EG module and select the module serial number on the drop down menu (General tab). Enter the cartridge serial number on EGC-1 (Cartridge tab), and link the EGC-1 to Pump 1. Add the AS-HV module and select *COM 1* (General tab). Select *15 Position* for the Sample Rack, *Internal Peristaltic Pump* for Sample Loading Pump, *Sample Loop* for Sample Loading Type, *Pull* for Sample Loading Mode, and enter the delay volume in mL (calculated volume of the green PEEK sample tubing from the needle to Port S in Inj. Valve 2) (Options tab). Check for errors in the configuration under Messages and check configuration program (Command, *Check*). Save the changes and close Chromeleon Configuration.

Controlling the Dionex AS-HV Autosampler with the Chromeleon panel and manual commands

To start the Chromeleon program, double click on the Chromeleon program icon and then click on the Panel Set icon. Select the AS-HV tab and enter 12 (mm) in Needle Height and 7.00 (mL) in Rinse Volume. Click on the Rinse command button to flush and prime the autosampler with the water from the 4 L flush container. Position numbers, R0, R1, etc., are displayed in the tray configuration diagram displays. For this autosampler, both the letter and the number are required to specify the position in the tray. For example, R0 is the rinse station

and R15 is the last position in this tray. The Dionex AS-HV Autosampler withdraws the total volume of the delay volume and the injection volume listed in the sequence from the sample bottle. To ensure that the sample loop and sample lines are sufficiently rinsed with the new sample, enter a number in the sequence that is 2.5 times the loop volume, e.g., 5 (mL) for a 2-mL injection.

To manually control the autosampler, press the F8 key on the keyboard (or Control, Command on Panel), select *Sampler*, the desired function, and press *Execute*. A Reset command re-aligns the autosampler arm to all four corners of the tray table. Reset is used when the needle or arm becomes misaligned, a needle is installed, or the tubing gets caught and stops or misaligns the needle. A *Rinse* command moves the needle to the R0 position (*Rinse Reservoir*) and rinses the needle and the sample line with 7 mL of deionized water at 1.2 mL/min from the 4 L external water container. *NeedleHome* and *NeedleDown* are up and down commands. *Internal-PumpOn* and *InternalPumpOff* turn the peristaltic pump on and off. More information on manual commands can be found in the autosampler manual.[11]

Creating the program with Chromeleon wizard
To create a program with Chromeleon Wizard, enter the values listed in the Conditions section and Table 2. Enter the Dionex AS-HV Autosampler values [Needle Height, Rinse Volume (mL), and Flow Rate values] and select *InjectValve_2* in Valve Control in the Sampler Options section. To select Sample Overlap mode, check the box and enter 10 (min) in the Delay Before Processing Next Sample slot. Sample Overlap mode is useful because it reduces total run time by preparing the next sample while the first sample is running. In lower volatility solvents, such as methanol and ethanol, sample overlap is suitable. Sample Overlap is not recommended for more volatile solvents, such as acetone, because the sample evaporates before it can be injected, generating low results. (To deselect Sample Overlap, uncheck the box.) In the Relay and State Devices Options tab,

Table 2. Eluent conditions for Chromeleon software

Time	KOH Concentration (mM)	Commands	Description
-2.0	22		Starts the 7 min (-2 to 5 min) equilibration on System 1.
0.0	22	Inj. Valve 2: Load	Loads the sample into sample loop (System 2) in Pull mode.
0.0	22	Inj. Valve 2: Inject Inj. Valve 1: Load	Pump 2 rinses the sample from the sample loop to the System 1 concentrator column in sample load and starts the matrix elimination process. (The concentrator traps the trace anions while Pump 2 rinses the solvent to waste.)
5.0[a]	22	Inj. Valve 1: Inject	Matrix elimination ends, equilibration ends, and the trace anions are injected onto the analytical system.
5.0[a]	22	CD_1.AcqOn CD_1_Total.AcqOn (Move these commands from time zero)	Start data acquisition.
10[a]	22	PrepareNextSample OR Position=R0 GotoPositionRinse	Start preparing the next sample for injection while in Sample Overlap mode. The preparation includes a 7 mL rinse step. Add these rinse commands if sample overlap mode is turned off. Start gradient eluent conditions.
25[a]	48		End gradient eluent conditions. Start isocratic conditions.
35[a]	48		End isocratic eluent conditions.
35[a]	65		Start column wash.
40[a]	65		End column wash and program.

[a]For NMP analysis, add five min to the injection time, and shift all subsequent times by five min (e.g., 5.0 becomes 10.0, 10.0 becomes 15.0)

enter the valve commands for Inj. Valve 1 by selecting *InjectValve_1,* LoadPosition, enter 0 (min) in the Retention Time, and click on *Add*. Repeat the commands using *InjectPosition,* and enter 5 (min). After the program is completed, select *Review Program* and click on *Finish*. When the program is displayed, deselect the Duration commands next to Inj. Valve 1 commands by entering a semicolon in front of the Duration =. Move the acquisition commands, *CD_1.AcqOn* and *CD_1_Total.AcqOn,* from time = 0 to time = 5 (min) to coincide with the 5 min injection time by cutting (Edit, Cut) and pasting (Edit, Paste). These times and commands are listed in Table 2. Review and check the program by selecting *Control, Check.* Save the program.

Calculations

Calibration curves

In trace analysis, it is critical that the calibration standards fit on the calibration curve especially at the low end of the calibration curve because most of the sample results will occur at the low end. To check for the fit, expand the low end of the calibration curve to view the relationship of the points to the curve. If the points are not on calibration line, the fit can often be improved by removing the highest concentration standard from the calibration curve to reduce the calibration range, or by using $1/x$ or $1/x^2$ weighting. Select the best fit to the low end of the calibration curve.

Water blanks

In trace analysis, the limiting factor to the limits of detection are the concentrations measured in the water blank. To determine the blank concentration, the baseline and the blank concentration must be reproducible for three injections. Continue to equilibrate the IC system and inject blanks until both are stable. The reported blank concentration is calculated by the averaging the last three reproducible water blank injections.

Reported blank = average (blank 1, blank 2, blank 3)

Samples

The blank must be subtracted from the measured results, especially at concentrations near the lower end of the calibration curve.

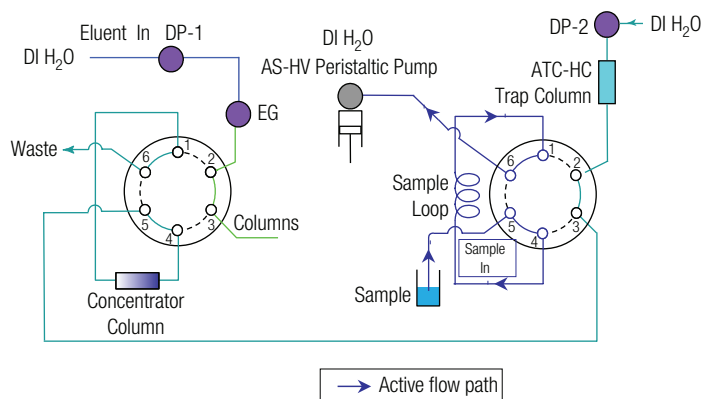Reported concentration = (measured concentration) minus (reported blank concentration)

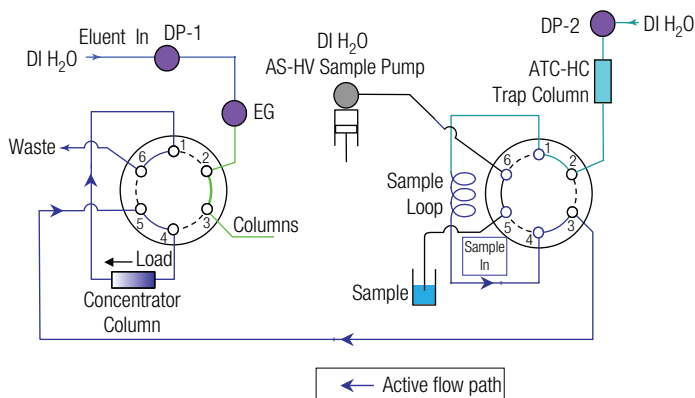Figure 3. Dionex AS-HV Autosampler peristaltic pump pulling sample into the sample loop

Figure 4. Preconcentration of trace ions and solvent matrix elimination
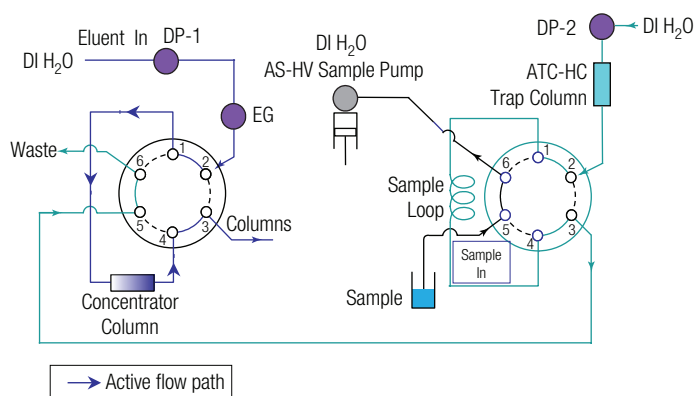

Figure 5. Retained anions eluted from the concentrator column onto the analytical column

Recovery samples

Recovery samples were prepared gravimetrically (instead of volumetrically) to increase measurement accuracy. In this application update, the samples are solvents with densities (Table 3) smaller than water (assume 1.0 g/mL at room temperature). For analysis of samples, it is not necessary to correct for density. However, for recovery determinations it is necessary to correct for density when standard is added to samples.

Table 3: Sample densities

Sample	Density (g/mL)
2-Propanol	0.786
Methanol	0.792
Acetone	0.784
NMP	1.03

Corrected density results for sample with standard = (measured concentration after adding standard minus blank) x density

Corrected density results for sample = (measured concentration minus blank) x density

Corrected density results for standard added to sample = standard concentration x density

% Recovery = Corrected measured results of sample with standard / ((corrected results of sample) + (corrected results for standard added to sample))

Results and discussion

This application uses both systems of the Dionex ICS-3000 RFIC system in a four step process: 1) loading the sample into the sample loop in pull mode, 2) transferring the sample into the concentrator column, 3) eliminating the solvent matrix from the concentrator, and 4) eluting the anions from the concentrator onto the analytical column. InStep 1 (Figure 3), the peristaltic pump of the Dionex AS-HV Autosampler pulls a 5 mL sample from the sample bottle at 1.2 mL/min through the sample line, and loads the sample into the 2 mL sample loop on System 2. The Dionex AS-HV Autosampler is operated in pull mode to minimize any possible contamination from the AS-HV. The sample is exposed only to the HDPP sample bottle, bottle septa, PEEK needle, and PEEK sample tubing as it is loaded into the sample loop. In Step 2 (Figure 4), Pump 2 delivers the sample onto the System 1 Dionex

Sample Prep.
Trap Column: Dionex IonPac ATC-HC
Carrier: Deionized water
Matrix Elimination: 10 mL
Flow Rate: 2 mL/min
Inj. Volume: 2 mL
Load Volume: 5 mL
AS-HV Rinse Vol.: 7 mL
AS-HV Mode: Peristalitic Pump, Pull

Analytical
Column: Dionex IonPac AG18, AS18, 2 mm
Eluent: 22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source: Dionex EGC II KOH
Flow Rate: 0.25 mL/min
Temperature: 30 °C
Detection: Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator: Dionex IonPac UTAC-ULP1

Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Lactate ND
4. Chloride <0.11
5. Nitrite ND
6. Carbonate ND
7. Sulfate <0.18
8. Nitrate <0.45
9. Phosphate <0.20

*ND = not determined

Figure 6. Chromatogram of a water blank

IonPac UTAC concentrator column using a deionized water carrier at 2.0 mL/min. In Step 3 (Figure 4), Pump 2 flushes the solvent to waste at 2.0 mL/min with deionized water while the trace anions are retained on the concentrator column. Steps 2 and 3 occur during the five min from time = 0 to time = 5 min, when the sample is injected. In Step 4 (Figure 5), the trace anions are eluted from the concentrator column at 5 min, separated on the Dionex IonPac AS18 2-mm column, and detected by suppressed conductivity. Data acquisition starts at 5 min, when the sample is eluted from the concentrator. In trace anion determinations, the carbonate peak dominates the chromatogram and interferes with the quantification of sulfate and neighboring anions. To eliminate this interference, a Dionex CRD 200 device is installed between the suppressor and the detector to remove the carbonate from the sample before detection. See Technical Note 62[13] for more information on the Dionex CRD (now the CRD 200 device).

Table 4. Method detection limits and SEMI specifications

Anion	2-Propanol MDL[a] (µg/L)	SEMI Specifications			
		2-Propanol Grade 4[b] (µg/L)	Acetone Grade 1[c] (µg/L)	Methanol Grade 1[d] (µg/L)	N-Methyl-2-Pyrrolidone Grade 3[e] (µg/L)
Chloride	0.105	<50	<200	<200	<300
Sulfate	0.178	<50	–	<500	<250
Nitrate	0.448	<50	<100	–	<400
Phosphate	0.200	<50	–	–	<250

n = 5

[a]Method detection limit based on least squares regression analysis in alcohol matrix according to SEMI C10-0305[14]

[b]SEMI specification C41-0705 (isopropyl alcohol)1[15]

[c]SEMI specification C19-0301 (acetone)[16]

[d]SEMI specification C31-0301 (methanol)[17]

[e]SEMI specification C33-031 (N-Methyl-2-Pyrrolidone)

Anions were determined for the system blank and the 5 µg/L combined standard of chloride, sulfate, nitrate, and phosphate. The system blank was determined with a water injection from an HDPP sample bottle (Figure 6). The system blank had low concentrations of formate, lactate, and nitrite, as well as concentrations below the method detection limits (MDLs) of chloride, sulfate, and nitrate. The chromatogram of the 5 µg/L standard in water (Figure 7) shows good peak responses and peak shapes for chloride, sulfate, nitrate, and phosphate in water. The retention time stabilities were good, <1 %RSD (n = 5).

Method qualification

The matrix elimination method was qualified in deionized water and isopropyl alcohol solutions. The linearity of chloride, sulfate, nitrate, and phosphate over a 200-fold concentration range, typical noise, MDLs, reproducibilities, and spike recoveries were determined in isopropyl alcohol solutions. The linearities of peak responses for chloride, sulfate, nitrate, and phosphate were measured by determining each anion in four replicates each of the nine working standards (0.1, 0.2, 0.5, 1, 2, 5, 10, 20, and 50 µg/L). The calibration results showed good linearities over this concentration range: $r^2 > 0.999$.

The noise was determined by measuring the noise at 1 min intervals from 45 to 90 min after five injections of water. The noise value determined by this experiment was 2.2 ± 0.8 nS (n = 5). The MDL was determined using

Sample Prep.: As in Figure 6

Analytical
Column: Dionex IonPac AG18, AS18, 2 mm
Eluent: 22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source: Dionex EGC II KOH
Flow Rate: 0.25 mL/min
Temperature: 30 °C
Detection: Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator: Dionex IonPac UTAC-ULP1
Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Lactate ND
4. Chloride 4.99
5. Nitrite ND
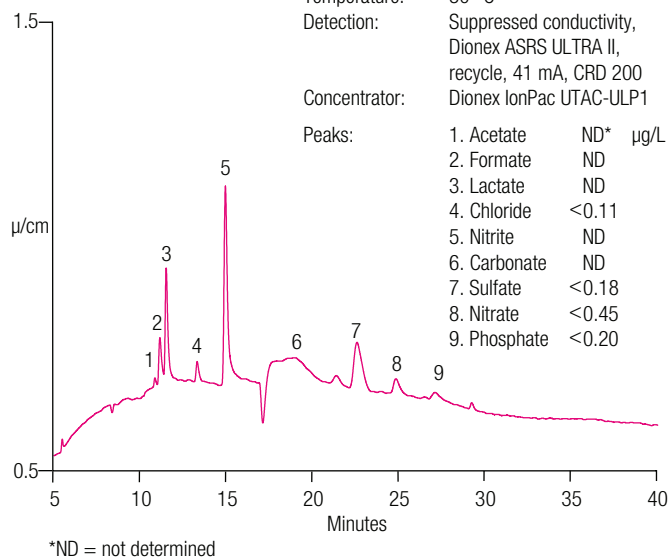6. Carbonate ND
7. Sulfate 5.08
8. Nitrate 5.34
9. Phosphate 4.95
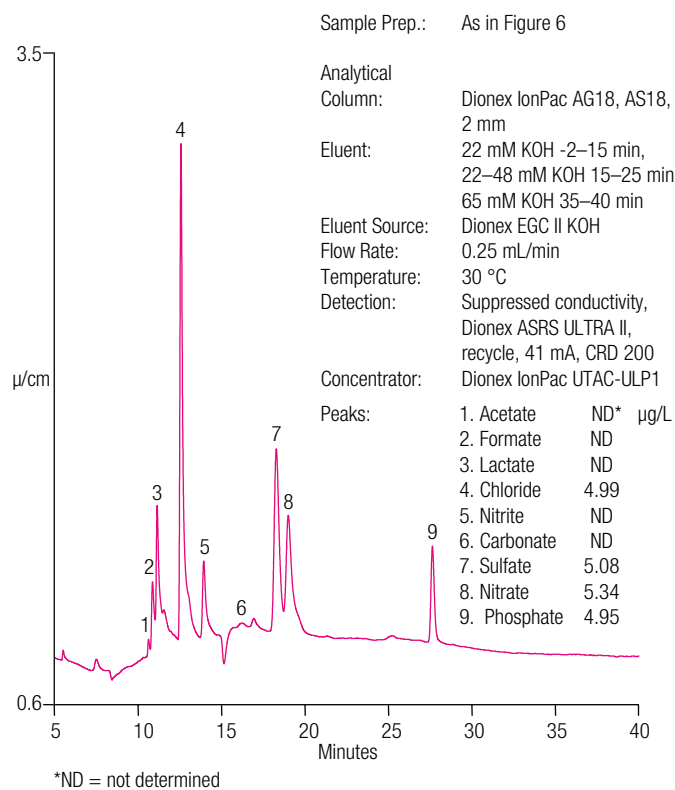
*ND = not determined

Figure 7. Chromatogram of a chloride, sulfate, nitrate, and phosphate standard, 5 µg/L each in water

the least squares method in the SEMI C10-0305 guide.[14] For this application, the MDL concentrations for the four analytes ranged from 0.11 to 0.45 µg/L (Table 4).

A 2.0 µg/L chloride, sulfate, nitrate, and phosphate standard in isopropyl alcohol had signal-to-noise

Table 5. Retention time and peak area reproducibilities of isopropyl alcohol spiked with 2 µg/L of each anion

Anion	Retention Time (min)	RSD	Peak Area (µS-min)	RSD
Chloride	12.53 ± 0.01	<0.02	0.305 ± 0.001	0.14
Sulfate	18.25 ± 0.01	0.03	0.150 ± 0.002	1.12
Nitrate	18.98 ± 0.01	0.02	0.246 ± 0.001	0.59
Phosphate	27.62 ± 0.01	<0.02	0.041 ± 0.001	2.71

n = 5

Table 6. Recoveries of anions in solvents

	2-Propanol		Acetone		Methanol		N-Methyl-2-Pyrrolidone	
Anion	Present (µg/L)	Recovered[a] (%)	Present (µg/L)	Recovered[b] (%)	Present (µg/L)	Recovered[b] (%)	Present (µg/L)	Recovered[b] (%)
Chloride	3.00 ± 0.03	100	<MDL	101.8	0.60 ± 0.01	99.3	9.49 ± 0.37	101.0
Sulfate	1.88 ± 0.03	89.5	5.02 ± 0.05	101.6	<MDL	106.4	35.15 ± 1.07	98.2
Nitrate	1.34 ± 0.05	106	<MDL	19.3	1.55 ± 0.14	98.4	26.75 ± 0.34	103.1
Phosphate	<MDL	87.3	2.86 ± 0.11	96.0	<MDL	94.1	22.90 ± 0.41	105.7

n = 5

<MDL = below method detection limit

[a]Spiked with 2.0 µg/L of chloride, sulfate, nitrate, and phosphate

[b]Spiked with 10.0 µg/L of chloride, sulfate, nitrate, and phosphate

ratios of 365 ± 133, 112 ± 40, 50 ± 18, and 5.7 ± 2.1, respectively. The MDL concentrations with this method are significantly lower (100–2,800 fold) than those needed for the SEMI specifications[15–18] and 4–5 fold lower than previously reported in AN85. The lower detection limits are a result of using an RFIC system, and the low noise of suppressed conductivity detection of hydroxide eluent compared to the carbonate eluents used in AN85. Spike recovery and retention time and peak area reproducibilities were determined for 2.0 µg/L chloride, sulfate, nitrate, and phosphate added to isopropyl alcohol. The retention times were very stable, < 0.3% RSD (Table 5). The peak areas of chloride, sulfate, and nitrate had good reproducibility (< 1% RSD). Phosphate peak areas had higher variation; 2.7% RSD. The recoveries of all four analytes were good: 98.9 to 101.2%, n = 5 (Table 6).

Determination of trace anions in methanol and acetone

The matrix elimination method was used to determine trace anions in isopropyl alcohol, acetone, and methanol, and in spiked samples of these solvents. Unspiked isopropyl alcohol, acetone, and methanol had trace concentrations of chloride, sulfate, nitrate, and phosphate, ranging from non-detectable to <5 µg/L (Table 6). Spike recoveries of 2 µg/L of chloride, sulfate, and phosphate in isopropyl alcohol, acetone, and methanol were good, 92.5–101.2, 96.1–101.8, and 94.1–106.4%, respectively. Nitrate had acceptable recoveries in isopropyl alcohol, and methanol (92.5–98.2), but the recovery of nitrate in acetone was poor, 19.3%. The cause of this poor recovery is unknown.

The chromatography of unspiked and spiked isopropyl alcohol (Figures 8–9), unspiked acetone (Figure 10), and unspiked and spiked methanol (Figures 11–12) were acceptable. The earlier peaks had good peak shape. The sulfate peak was typically wider than desired. The peak dip in front of the carbonate peak is due to removal of carbonate by the CRD 200 and the resultant drop in conductivity.
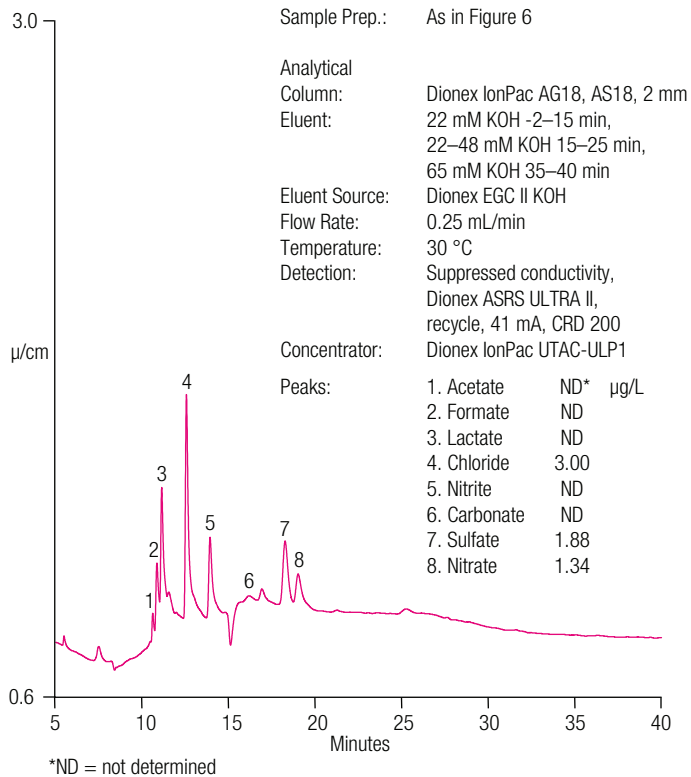
Figure 8. Chromatogram of unspiked 100% 2-propanol

Sample Prep.: As in Figure 6

Analytical Column:	Dionex IonPac AG18, AS18, 2 mm
Eluent:	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source:	Dionex EGC II KOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator:	Dionex IonPac UTAC-ULP1

Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Lactate ND
4. Chloride 3.00
5. Nitrite ND
6. Carbonate ND
7. Sulfate 1.88
8. Nitrate 1.34

*ND = not determined

Figure 9. Chromatogram of a chloride, sulfate, nitrate, and phosphate standard, 5 µg/L each, spiked in 2-propanol

Sample Prep.: As in Figure 6

Analytical Column:	IonPac AG18, AS18, 2 mm
Eluent:	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source:	EGC II KOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, ASRS® ULTRA II, recycle, 41 mA, CRD 200
Concentrator:	IonPac UTAC-ULP1

Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Lactate ND
4. Chloride 5.03
5. Nitrite ND
6. Carbonate ND
7. Sulfate 3.09
8. Nitrate 3.08
9. Phosphate 1.80

*ND = not determined

Figure 11. Chromatogram of unspiked 100% methanol

Sample Prep.: As in Figure 6

Analytical Column:	Dionex IonPac AG18, AS18, 2 mm
Eluent:	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source:	Dionex EGC II KOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator:	Dionex IonPac UTAC-ULP1

Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Lactate ND
4. Chloride 0.60
5. Nitrite ND
6. Carbonate ND
7. Sulfate <0.18
8. Nitrate 1.55

*ND = not determined

Figure 10. Chromatogram of unspiked 100% acetone

Sample Prep.: As in Figure 6

Analytical Column:	Dionex IonPac AG18, AS18, 2 mm
Eluent:	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source:	Dionex EGC II KOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator:	Dionex IonPac UTAC-ULP1

Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Chloride <0.11
4. Sulfate 5.02
5. Phosphate 2.86

*ND = not determined

Determination of trace anions in N-methyl-2-pyrrolidone (NMP)

The initial evaluations of NMP with this method showed that the solvent carried over into the analytical column (System 1). To eliminate this, five min were added to the matrix elimination step. The anions from NMP were injected at 10 min, and hence all subsequent program steps were shifted 5 min. Figure 13 shows the spiked NMP using the 10 min matrix elimination step. Chloride and phosphate had good peak shapes. Sulfate and nitrate peaks were wider than desired. Unspiked NMP had higher concentrations of the four anions than the other solvents, 9.49 ± 0.37 to 35.15 ± 1.07 µg/L (Table 5). The recoveries of 10 µg/L chloride, sulfate, and phosphate were similar to those for the other solvents, 98.2–105.7%. Nitrate recovery was 103.1%.

Sample Prep.:	As in Figure 6
Analytical	
Column:	Dionex IonPac AG18, AS18, 2 mm
Eluent:	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source:	Dionex EGC II KOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator:	Dionex IonPac UTAC-ULP1
Peaks:	1. Acetate ND* µg/L
	2. Formate ND
	3. Lactate ND
	4. Chloride 2.58
	5. Nitrite ND
	6. Carbonate ND
	7. Sulfate 2.02
	8. Nitrate 3.44
	9. Phosphate 1.89

*ND = not determined

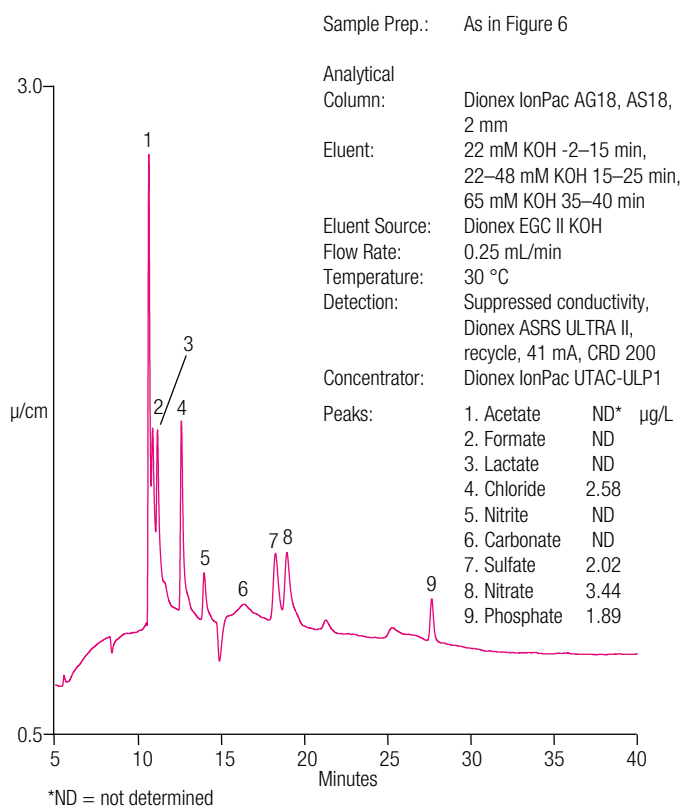**Figure 12. Chromatogram of a chloride, sulfate, nitrate, and phosphate standard, 2 µg/L each, in methanol**

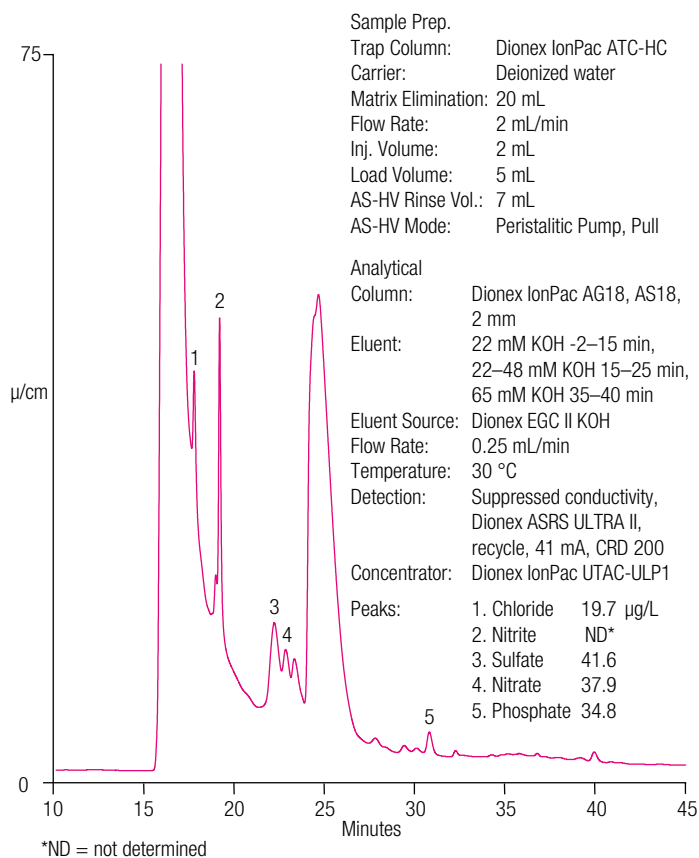| Sample Prep.	
Trap Column:	Dionex IonPac ATC-HC
Carrier:	Deionized water
Matrix Elimination:	20 mL
Flow Rate:	2 mL/min
Inj. Volume:	2 mL
Load Volume:	5 mL
AS-HV Rinse Vol.:	7 mL
AS-HV Mode:	Peristaltic Pump, Pull
Analytical	
Column:	Dionex IonPac AG18, AS18, 2 mm
Eluent:	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Eluent Source:	Dionex EGC II KOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, recycle, 41 mA, CRD 200
Concentrator:	Dionex IonPac UTAC-ULP1
Peaks:	1. Chloride 19.7 µg/L
	2. Nitrite ND*
	3. Sulfate 41.6
	4. Nitrate 37.9
	5. Phosphate 34.8

*ND = not determined

Figure 13. Chromatogram of a chloride, sulfate, nitrate, and phosphate standard, 10 µg/L each, in N-methyl-2-pyrrolidone using a 10-min matrix elimination sample preparation

Conclusion

This application update demonstrates that µg/L anion concentrations can be determined in 2 mL samples of the water miscible solvents isopropyl alcohol, methanol, acetone, and N-methyl-2-pyrrolidone after matrix elimination of the solvent. This matrix elimination can be fully automated using a Dionex AS-HV Autosampler and dual pump, dual valves in the DC, and eluent generation of a Dionex ICS-3000 system; no lengthy sample preparation is required. The matrix elimination occurs automatically as the sample is transferred from System 2 to System 1 within the Dionex ICS-3000 DC lower chamber. The setup described here is an easy, automated, and reproducible method to determine µg/L anion concentrations in water miscible solvents.

Precautions

Always use proper safety precautions when handling solvents. Consult the Material Safety Data Sheets (MSDS) for protective clothing, storage, disposal, and health effects. The waste effluent contains solvent and can not be discarded directly in the sink. Consult local safety regulations for proper disposal. Use only low-pressure concentrator columns, such as the Dionex IonPac UTAC-ULP1, tubing, and fittings with the AS-HV Autosampler in "pull" mode. Check and eliminate any restrictions to flow from the tubing and fittings on the Dionex AS-HV Autosampler, System 2, and the sample loop. Restrictions can interfere with the peristaltic pump flow. The Dionex AS-HV needle can become clogged with salts deposited by evaporating solvents. Periodically disassemble the Dionex AS-HV Autosampler needle and clean it in deionized water. Always use high quality deionized water (>18.2 MΩ·cm) for preparing reagents and samples.

Tighten the fittings on the Dionex Carbonate Removal Device (CRD 200) to finger-tight; do not over-tighten. Do not allow more than 100 psi system backpressure on the Dionex CRD 200 device and the Dionex ASRS ULTRA II suppressor because higher pressures can cause irreversible damage to these devices. The Dionex IonPac UTAC-ULP1 column may need to be replaced periodically when peak splitting or a drop in response is observed.

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