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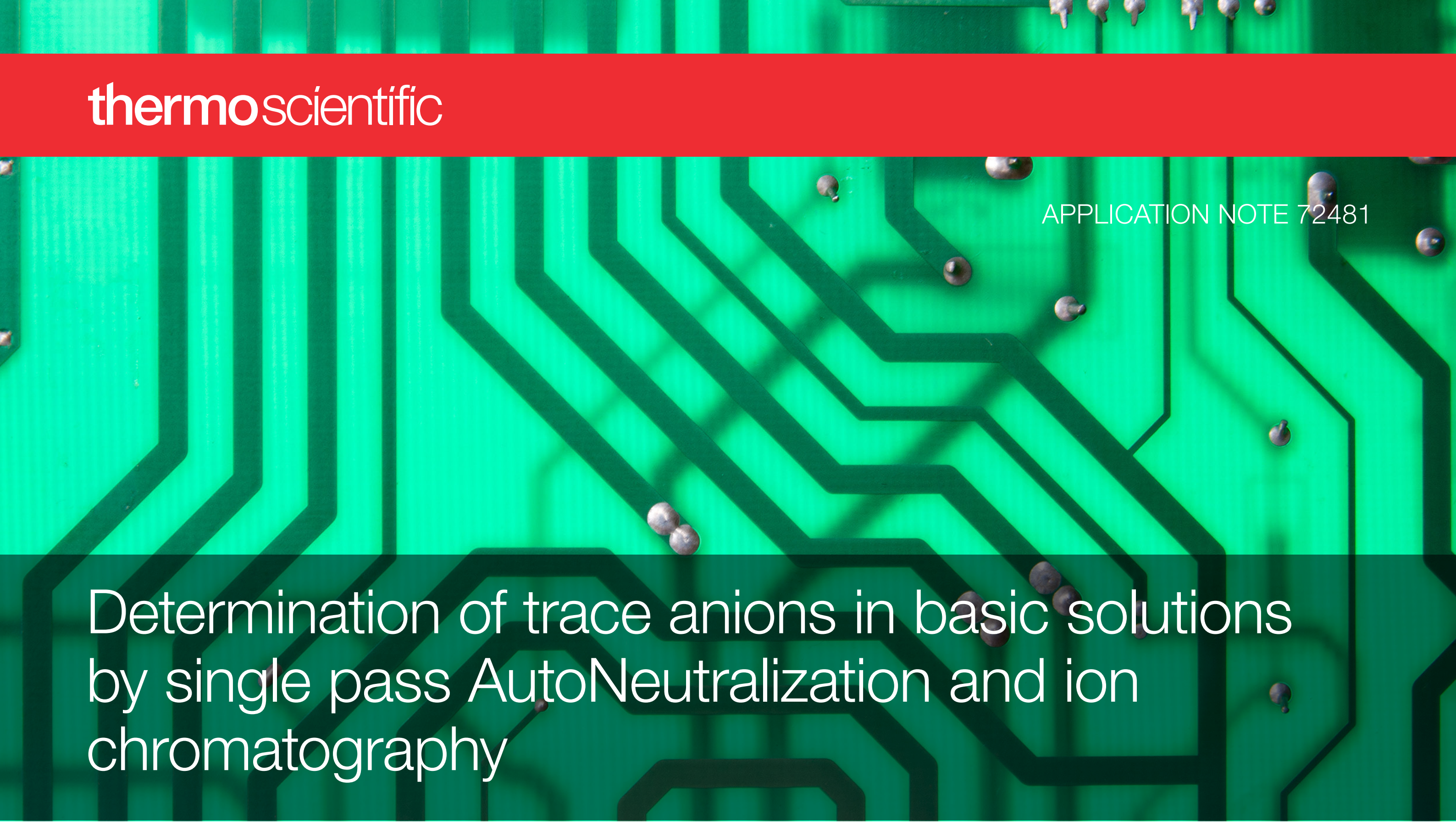

Determination of trace anions in basic solutions by single pass AutoNeutralization and ion chromatography

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Keywords

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Introduction

The electronics industries need analytical methods to determine trace anions in concentrated bases. Anions can cause corrosion, deposition defects, and electronic shorts in electronic devices, even at very low concentrations. Ion chromatography (IC) with suppressed conductivity detection is the preferred and well-established method for determining ionic species, especially at µg/L and ng/L concentrations.

Direct analysis of concentrated base samples is challenging because the high concentrations of the base anion overloads the column, resulting in poor chromatography and quantification. Diluting the concentrated bases prior to anion analysis mitigates the column overload issue. However, this dilution sacrifices anion determinations at µg/L and ng/L concentrations. The introduction of AutoNeutralization™ by Dionex in 1994, embodied in the SP10 AutoNeutralization module, eliminated the need to dilute the concentrated base and thus allowed µg/L and ng/L anion determinations.[1] This technique used multiple cycles through the neutralizer to completely neutralize the strong acid or base in the sample. The second embodiment of AutoNeutralization replaced the SP10 with two, six-port valves and an external pump installed on the Dionex ICS-2500 chromatography system.[2]

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This method, reported in the previous version of this application note,[2] effectively neutralized strong bases with a series of neutralizing cycles. This same technique was used to neutralize acids.[3] In the latest versions of AutoNeutralization, the sample was pumped into the Thermo Scientific™ Dionex™ ASRN™ II Anion Self-Regenerating Suppressor™ by an external pump and trapped for a set period. This technique was coined Park and AutoNeutralize.[4] This technique was also applied to analyzing trace anions in volcanic gas condensates.[5]

Here we discuss a Single Pass AutoNeutralization by using the high static capacity of a 4 mm Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor to neutralize the base samples in a single pass. The 4 mm Dionex AERS 500 suppressor replaces the previously used Dionex ASRN II Anion Self-Regenerating Neutralizer, which required multiple passes or holding ("parking") the sample in the neutralizer.

The single pass approach has been demonstrated with both suppressors run in recycle mode (Figure 1, page 6) or in external water mode (Figure 2, page 8) with a third pump.[6] The suppressor recycle mode has the advantages of further eliminating the need for extra bottles or pumps. The previously used Thermo Scientific™ Dionex™ IonPac™ AS19 column is updated with Thermo Scientific™ Dionex™ IonPac™ AS18-4µm column for faster separations of inorganic anions and higher resolving power of sulfate from the carbonate peak, thereby eliminating the need for a carbonate removal device. However, the 4 µm resin beads result in higher operating pressures than 3,000 psi, thereby requiring updates to high pressure capable Reagent-Free™ IC (RFIC™) eluent generator cartridges, suppressors, and IC systems. This application replaces AN93: Determination of Trace Anions in Concentrated Bases Using AutoNeutralization Pretreatment and Ion Chromatography (Park and AutoNeutralize), published in 2007.[5]

Experimental

Chromatography instrument

This single pass AutoNeutralization application is supported on two IC system platforms: the Thermo Scientific™ Dionex™ ICS-5000+ HPIC chromatography system in 1a) recycle mode and 1b) external water mode, 2) the Thermo Scientific™ Dionex™ Integrion™ HPIC™ chromatography system. In this application note, the Single Pass AutoNeutralization method is demonstrated on the Dionex ICS-5000+ HPIC chromatography system in recycle mode using two injection valves, pumps (in recycle mode, (1a)), CD conductivity detectors, and suppressors.

1a. Dionex ICS-5000+ HPIC chromatography system with suppressors in recycle mode (Figure 1, page 6), including

- – SP Single Pump module
- – EG Eluent Generator module
- – DC Detector Column Oven module with two high pressure injection valves
- – Two CD Conductivity cells (for suppressed conductivity detection and to monitor neutralization)*

*The second CD detector is optional but useful when optimizing the method timing (Setup section, *Determining the timing for AutoNeutralization*)

- Thermo Scientific™ Dionex™ AXP Auxiliary Pump, (P/N 063973), pumps deionized (DI) water through a Thermo Scientific™ Dionex™ IonPac™ ATC-HC 500 trap column that removes trace anions, to transfer the sample from the sample loop to the neutralizing suppressor (4 mm Dionex AERS 500 suppressor) and to the concentrator column.
- Thermo Scientific™ Dionex™ AS-AP Autosampler with 10 mL sample vial tray holders

1b. Dionex ICS-5000+ HPIC chromatography system with neutralizing suppressor in external water mode (Figure 2, page 8) including

- – Same modules listed in 1a
- – Add a second AXP pump to provide external water at 1 mL/min DI water for the neutralizing suppressor

2. Dionex Integrion HPIC system with consumables monitoring (P/N 22153-60305) includes:
   - Eluent generation
   - Column oven temperature control
   - Detector-Suppressor compartment temperature control
   - Tablet control
   - Consumables Monitoring
   - RFIC EG Degas module

- Dionex Integrion Auxiliary Power Supply Control option, P/N 22153-62023, to power the neutralizing suppressor
- Dionex Integrion CD Conductivity Detector, P/N 22153-62034
- Dionex Integrion HPIC Mobile Instrument Control option and tablet
- Additional 6-Port Injection Valve, P/N 22153-62027
- Dionex AXP Auxiliary Pump, (P/N 063973), pumps DI water through Dionex IonPac ATC-HC 500 trap column, which removes trace anions, to transfer the sample from the sample loop to the neutralizing suppressor (4 mm Dionex AERS 500 suppressor) and to the concentrator column.
- Dionex AS-AP Autosampler with 1 mL syringe and 10 mL sample vial tray holders

Software

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) 7.2, SR4 software

Table 1. Consumables needed for this application.

Product Name	Description	Part Number
Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge	Eluent generator cartridge recommended for this application	075778
Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column	Dionex CR-ATC 500 trap column is used with Dionex EGC KOH 500 cartridge on the Dionex ICS-5000$^+$ systems	075550
	Dionex CR-ATC 600 trap column is used with Dionex EGC KOH 500 cartridge on the Dionex Integrion RFIC systems	088662
Thermo Scientific™ Dionex™ HP Degasser Module	Degasser installed after Dionex CR-TC trap column and before the Injection Valve. Used with eluent generation	075522
Thermo Scientific™ Dionex™ AERS 500 Anion Electrolytically Regenerated Suppressor	4 mm suppressor to neutralize the caustic samples, plumbed in recycle mode	082540
	2 mm suppressor for suppressed conductivity detection, plumbed in recycle mode	082541
Thermo Scientific™ Dionex™ IonPac™ AG18-4µm, AS18-4µm Column Set	Anion guard (2 × 30 mm) and separation column (2 × 150 mm) for fast separations	076037 / 076036
Thermo Scientific™ Dionex™ IonPac™ AG28-4µm and AS28-4µm Column Set	Alternative column set (Figure 9) Anion guard (2 × 30 mm) and separation column (2 × 150 mm) for higher resolution separations.*	088750 / 088749
Thermo Scientific™ Dionex™ CRD 200 Carbonate Removal Device, 2 mm	Used with 2 × 150 mm Dionex IonPac AS28-4µm column (Figure 11)	062986
Dionex ATC-HC 500 Anion Trap Column	Trap column (9 × 75 mm) on AXP pump. Used to purify the DI water passing through the pump. The purified DI water is used to transfer the sample from the sample loop to the neutralizing suppressor and the concentrator column	075978
Thermo Scientific™ Dionex™ IonPac™ UTAC-LP2 Ultratrace Anion Concentrator Column	Anion concentrator column to collect and concentrate the trace anions after neutralization, 4 × 35 mm	079917
Dionex AS-AP Autosampler Sample Vials	10 mL polystyrene vial kit, caps and blue septa	074228
Dionex External Regenerant Kit	Includes a 4 L bottle, tubing, ferrules, and connectors to install the neutralizing suppressor	038018

* The 2 mm Thermo Scientific™ Dionex™ IonPac™ AG19/AS19 column has been also previously demonstrated on this application[6] (P/N 062888/062886)

Conditions	
Columns:	Dionex IonPac AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
Gradient:	KOH gradient, 23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min), 45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min), 23 mM (8.1–12 min)
Eluent Source:	Dionex EGC 500 KOH Eluent Generator cartridge, Dionex CR-ATC 500 Anion Trap Column (CR-ATC 600 for the Integrion IC system) and high pressure degas module
Flow Rate:	0.25 mL/min
Injection Vol.:	100 µL
Column Temp.:	30 °C
Sample Prep.	
Transfer Water:	Dionex AXP pump at 1 mL/min (Figures 3–7, 9, 10) with Dionex IonPac ATC-HC 500 Anion Trap Column, 9 × 75 mm Dionex AXP pump at 0.5 mL/min (Figures 7 and 8) with Dionex IonPac ATC-HC 500 Anion Trap Column, 9 × 75 mm
Auto-Neutralization:	Single pass, Dionex AERS 500 Anion Electrolytically Regenerated Suppressor, 4 mm, recycle mode
Neutralizing Suppressor Current:	A: 300 mA for amine solutions (Figures 3–7, 9, 10) B: 490 mA for strong base solutions (Figures 7 and 8)
Concentrator:	Dionex UTAC-LP2, 4 × 35 mm

Conditions (continued)	
Compartment Temp.:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500 Anion Electrolytically Regenerated Suppressor, 2 mm, 28 mA, recycle mode
Run Time:	12.5 min
Background conductance:	< 1 µS
Noise:	~ 1 nS
System Backpressure:	~ 3,000 psi

Reagents

- ASTM™ Type I deionized (DI) water[7]
- Thermo Scientific™ Dionex™ Combined Seven Anion Standard II solution (P/N: 057590)

Samples

- 25% (w/w) Tetramethylammonium hydroxide (TMAOH, ($C_4H_{13}NO$), semiconductor grade
- Sodium hydroxide, 5%, 10% and 25% (w/w) prepared from 50% (w/w) sodium hydroxide solution, reagent grade, Thermo Scientific™ Acros Organics™, P/N: 259860010
- 0.1 M Tetrabutylammonium hydroxide (TBAOH, ($(C_4H_9)_4NOH$), ACS grade

Standard preparation

Degassed Type I DI water is prepared by vacuum filtration with applied ultrasonic agitation.

Five standards were prepared by diluting the Dionex Combined Seven Anion Standard II (20 mg/L fluoride, 100 mg/L chloride, bromide, nitrate, nitrite, sulfate, and 200 mg/L phosphate) with ASTM Type I DI water. To prepare 100 mL of an Intermediate Standard (0.2 mg/L fluoride, 1 mg/L chloride, bromide, nitrate, nitrite, sulfate, and 2 mg/L phosphate), tare the balance with a 125 mL HDPP or HDPE bottle. Pipette 1.0 mL of the Dionex Combined Seven Anion Standard II, add DI water to 100 g total, cap and shake the bottle to thoroughly mix the solution.

Prepare 100 mL solutions of Working Standards 1, 2, 3, 4, and 5 by pipetting 20, 100, 200, 400, 1,000 µL of the Intermediate Standard, respectively into individual 125 mL labeled bottles. Standard 0 is Type I DI water without an addition of intermediate standard. Dilute each one to 100.0 g total with DI water and thoroughly shake to mix the working standards. The final concentrations are shown in Table 2.

Setup

This application uses both systems of the high-pressure-capable Dionex ICS-5000^{+} HPIC dual system. System 1 has the same flow path as used in typical RFIC applications, whereas System 2 is used to load, transfer, neutralize the base sample and transfer the neutralized base sample to System 1 (Figure 1).

- **Load:** The Dionex AS-AP autosampler loads the base sample into the sample loop. If using another autosampler, a flush cycle may be required before the next injection. If using a manual injection, follow it with two full-syringe injections of DI water. Please note that other autosamplers and manual injections were not tested during this application work.
- **Transfer and neutralize with a single pass:** The Dionex AXP Auxiliary Pump delivers DI water at 1 mL/min through the Dionex IonPac ATC-HC 500 trap column to remove any impurities in the flow path. This cleaned DI water rinses the base sample from the sample loop into the 4 mm Dionex AERS 500 Anion Electrolytically Regenerating Suppressor in recycle mode using only a single pass. (The regenerant for the neutralizing suppressor is supplied by the waste line from Valve 1.) As the sample passes through the neutralizing suppressor, the sodium ions of the sample are exchanged with hydronium ions, thereby neutralizing the base.
- **Transfer and concentrate:** The neutralized sample, which is now a water solution with ppb concentrations of trace anions, continues on to System 1 to the Dionex IonPac UTAC-LP1 concentrator column (on Injection Valve 1, in the Load position). The trace anions are retained on the concentrator column while the water flows to waste. The timing for this step and the previous step is based on the AXP pump flow rate and length of tubing from the AXP pump to the neutralizing suppressor and to the concentrator column.
- **Elute, separate, and detect:** The trace anions are then eluted off the concentrator column (inject mode), separated on the guard and separation columns and detected by suppressed conductivity.

Table 2. Final concentrations of working standards.

	Concentration (µg/L, ppb)					
Anion	**Std 0 Blank**	**Std 1**	**Std 2**	**Std 3**	**Std 4**	**Std 5**
Fluoride	0	0.2	1.0	2.0	4.0	10.0
Chloride	0	1.0	5.0	10.0	20.0	50.0
Nitrite	0	1.0	5.0	10.0	20.0	50.0
Bromide	0	1.0	5.0	10.0	20.0	50.0
Sulfate	0	1.0	5.0	10.0	20.0	50.0
Nitrate	0	1.0	5.0	10.0	20.0	50.0
Phosphate	0	2.0	10.0	20.0	40.0	100.0

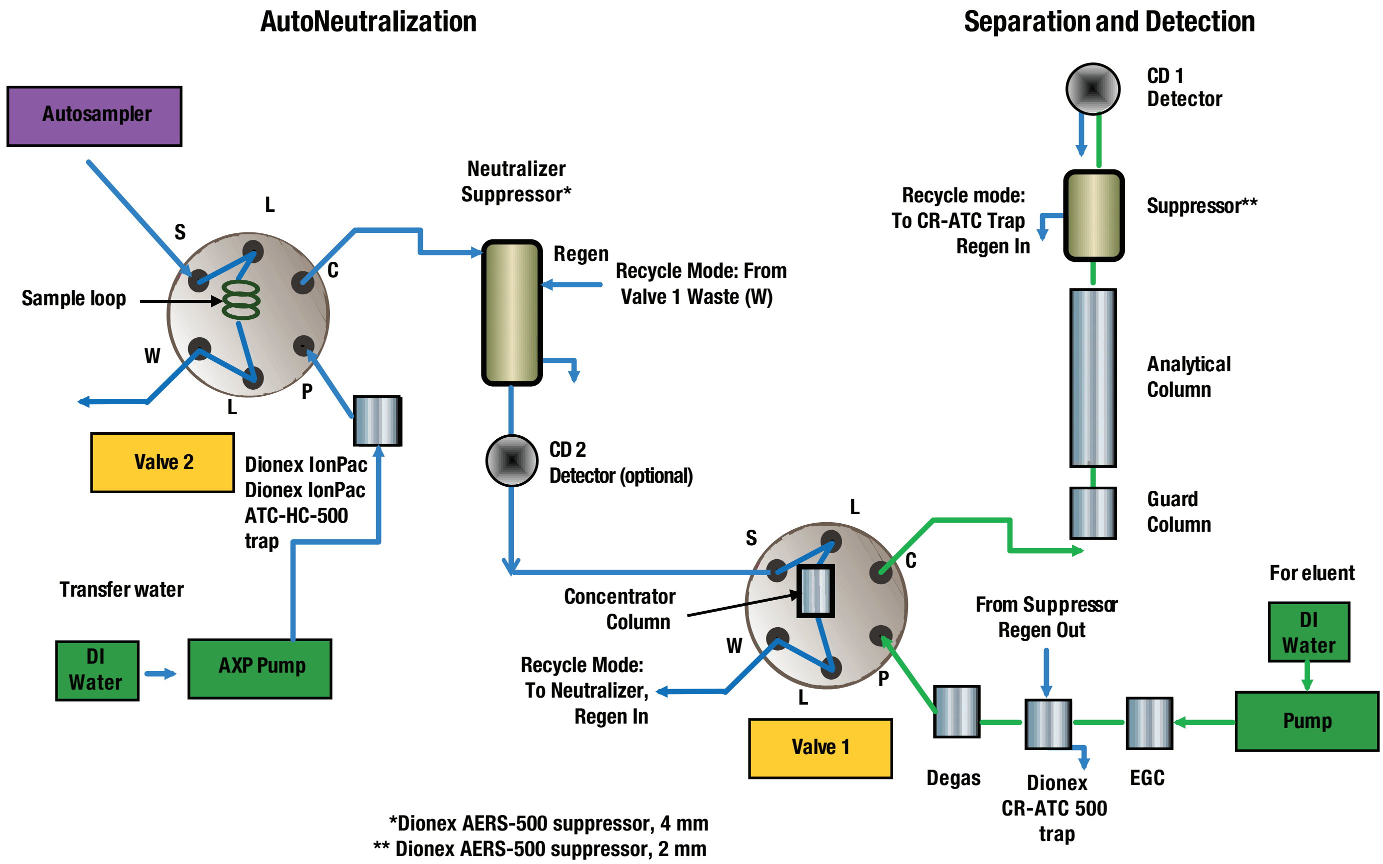

Figure 1. Flow diagram for AutoNeutralization in recycle mode.

To establish power and provide connectivity of the IC system, first install the CD detectors in System 1 and System 2, and the USB cables and power cables on the Dionex ICS-5000+ system modules, Dionex AS-AP autosampler, and computer. For the AXP pump, connect the serial-to-USB cables from the AXP pump directly to the computer. Turn on the modules and the computer. Start the Chromeleon Instrument Services Manager and Instrument Configuration programs. Create an Instrument configuration with the parameters described in Table 3.

Plumbing and conditioning the consumable devices

System 1

Plumb the System 1 flow path as shown on the right side of Figure 1 (from eluent pump to CD 1 detector with the 2 mm suppressor in recycle mode). Degas the DI water for the System 1 Dionex AXP Auxiliary Pump and the Dionex AS-AP Autosampler flush water using vacuum degassing. Prime the pumps until water is pumping without observable air bubbles.

Install and condition the Dionex EGC 500 KOH cartridge and CR-ATC 500 trap column according to the QuickStart instructions received with the devices and the product manuals.[8,9] Hydrate and condition the 2 mm Dionex AERS 500 suppressor with the power off by manually pushing 1 mL of DI water through the Regen In port and by pumping eluent (any concentration from “0” to 10 mM KOH) at 0.25 mL/min to the Eluent In position for 5 min. To minimize damage to the suppressor during hydration, do not add any backpressure tubing coils after the suppressor. To complete the hydration step, wait an additional 20 min without eluent flow before installing the suppressor in recycle mode. Connect Regen Out on the suppressor to Regen In on the Dionex CR-ATC 500 Anion Trap Column.

Table 3. Configuring the Dionex ICS-5000+ HPIC system with the Chromeleon CDS software.

Module	Tab	Action
SP	Device	Link Pump to Instrument.
EG	Cartridge	Link to Instrument, check EGC-1 for one cartridge, link to Pump_1
	General	Select instrument
DC	Detectors	Select CDet1, double-click on CDet1, Link to Pump_1, Check CD_1 and CD_1_total signal boxes.
		Repeat for CDet2 to link to Pump_2. Check CD_2_total
	Thermal Controls	Check Compartment_TC, and Column_TC
	Suppressors	Double click Suppressor1 (2 mm), Link to Pump_1. Repeat for Suppressor2 (4 mm), link to Pump_2.
	High Pressure Valves	Double click Inject on the valves. Assign control to AS for Valve_2 and to DC for Valve_1
	Low Pressure Valves	Remove check marks
AS-AP Autosampler	Sharing	Select only this instrument
	Segments / Pump Link	Select 10 mL PolyVials or 1.5 ml vials for “Red”, “Blue”, and “Green”
	Options	Select Push, select syringe size (1,000 µL), enter the loop size (100 µL)
	Relays	Remove check marks
	Links	Remove check marks
AXP Pump	Name	Change name to Pump2

Condition the columns: For the best chromatography, install the concentrator column with a short piece of tubing into Port 1 (between Port C and S) and a longer piece of tubing as needed in Port 4 (between Port P and W). Set Valve 1 to Inject. Condition the concentrator column at 45 mM KOH, 0.25 mL/min for 10 min while temporarily directing the flow from the columns to a waste container. Install and condition the guard and separation columns for 40 min (3 column volumes) using the same conditions. After conditioning is complete, connect the tubing at the separation column exit to the suppressor Regen In. Additional installation information is available in the product manuals and QuickStart Instructions.[8–13]

Plumb System 2 flow path as shown on the left side of Figure 1.

Condition the trap column by pumping DI water through the trap for 30 min with the flow directed to waste. Hydrate and condition the 4 mm Dionex AERS 500 Anion Electrolytically Regenerated Suppressor (neutralizing suppressor) with the power off by manually pushing 5 mL of DI water through the Regen In port and by pumping DI water at 1 mL/min to the Eluent In position for 5 min. To minimize damage to the neutralizing suppressor during hydration, do not add any backpressure tubing coils after the neutralizing suppressor. To complete the hydration step, wait an additional 20 min without eluent flow before installing the neutralizing suppressor in recycle mode. Do not install backpressure tubing coils received in the shipment kit as the backpressure tubing is not necessary for this application. Connect the waste line from Valve 1 to Regen In on the neutralizing suppressor. Direct the Regen Out line to a waste container. Install the 100 µL sample loop in the L ports of Injection Valve 2. Additional installation information is available in the product manuals and QuickStart Instructions.[8–13] Run both systems for at least one hour using the conditions listed in the Conditions section. For the best results, set Valve 1 in the “Inject” position and condition both systems overnight at the application settings.

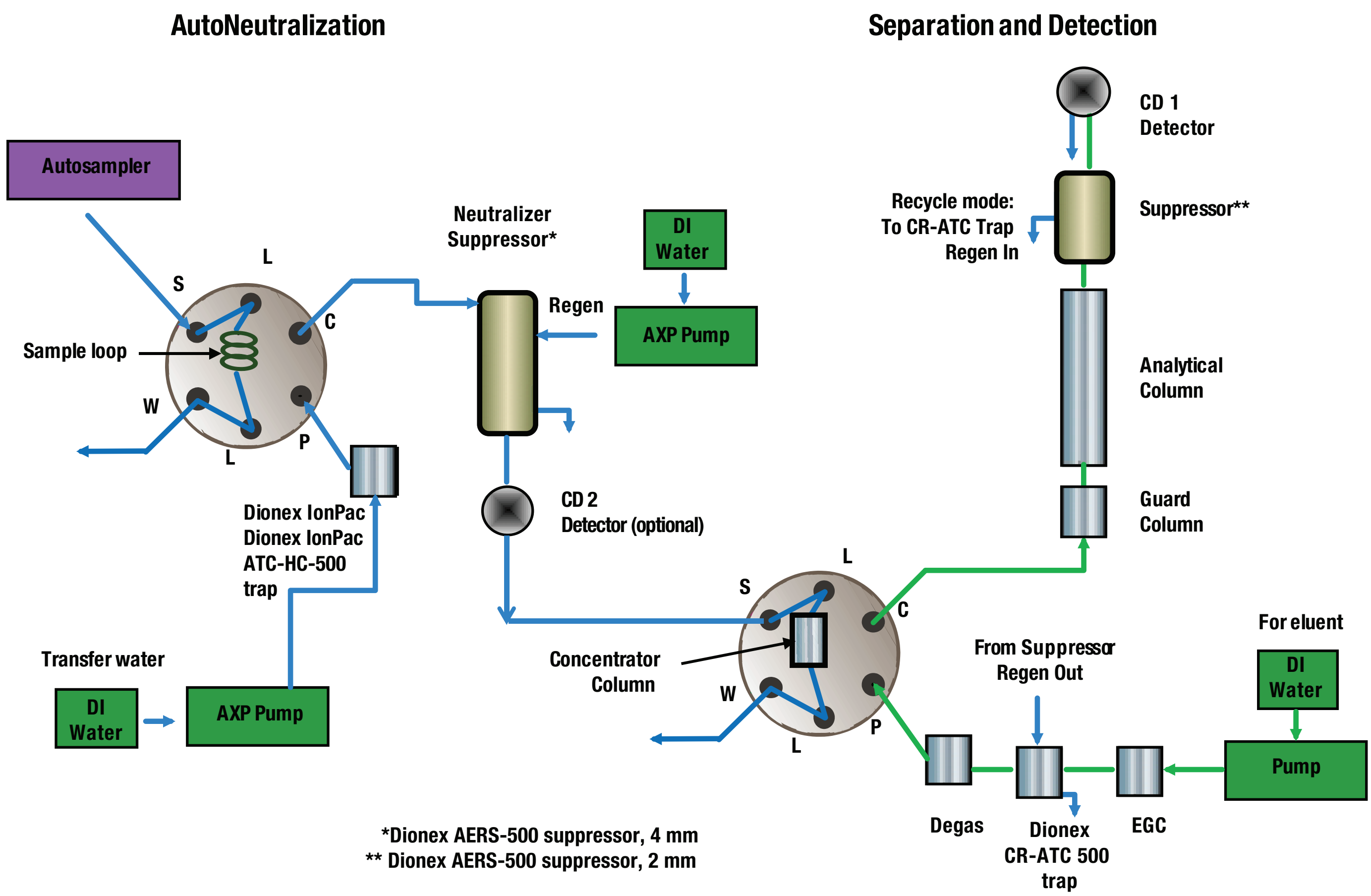

Figure 2. Alternative flow diagram using AutoNeutralization in external water mode.

Figure 2 shows an alternative configuration with the neutralizing suppressor in external water mode (chromatogram shown in Figure 11).[6]

To use the Dionex Integrion HPIC system for this application, install an additional power supply (Thermo Scientific service representative only) to power the neutralizing suppressor and a second six-port injection port according to Figure 1. Install the USB cables and power cables. Configure the Dionex Integrion HPIC system, two valves, two suppressors, autosampler, and Dionex AXP Auxiliary Pump with the Chromeleon CDS software. Items will automatically populate in the configuration. Follow the plumbing and conditioning instructions as described above. Then, install the 4 mm Dionex AERS 500 suppressor (neutralizing suppressor) in the EGC 2 position located on top of the Integrion near the Dionex EGC Eluent Generator Cartridge and Dionex CR-TC Continuously Regenerated Trap Column.

Chromeleon instrument program

Using the Chromeleon Wizard program, create an instrument method according the Table 4. Enter "242 mM KOH" as a temporary entry for the 4 mm suppressor to create 300 mA current, then manually enter "300" for amine samples or "490" for strong bases into the instrument method script. Review the script to ensure that the commands needed to time the valve switches are stated at the times in Table 4. The timing and eluent concentrations are entered in the gradient section of the Chromeleon Wizard program.

Determining the timing for AutoNeutralization

The time required to collect the neutralized sample is determined experimentally. Figure 3 shows the conductivity trace on CD2 channel which monitors the A) neutralized Standard 5, and B) neutralized 25% TMAOH sample. The experiments show that 0.40 min is sufficient. (Enter this value as a negative time (-0.40) in the Instrument Program at step "DC.InjectValve_1. LoadPosition".) The amount of time needed to collect the neutralized sample may be different on each system due to the length of tubing (Dionex AXP Auxiliary Pump to the Injection Valve 2 to neutralizing suppressor to concentrator column) and due to the sample viscosity and concentration.

Table 4. Additional timing commands to switch valves for single pass AutoNeutralization.

Time	Stage	Command	Action
-3.0	Equilibrium	DC.InjectValve_1.InjectPosition	Concentrator column is being washed with eluent
		23 mM KOH	Equilibrate at starting eluent concentration
-0.45		Sampler.Load	Loads sample
		Sampler.Inject	Injects sample
-0.40*		DC.InjectValve_1.LoadPosition	Concentrator column is ready to collect neutralized sample.
0	Start Run	DC.InjectValve_1.InjectPosition	Neutralized concentrated sample is injected onto the guard and separation columns
0	Run		
3.8		23 mM KOH**	Holds concentration at 23 mM KOH until 3.8 min, and starts the gradient
5.5		45 mM KOH**	Gradient reaches 45 mM KOH
8.0		45 mM KOH**	
8.1		23 mM KOH**	Start equilibrating at starting eluent concentration
12.0		23 mM KOH**	
12.5	Stop Run		

* See the section "Determining the timing for AutoNeutralization" for a discussion of the experiments to determine the timing for this step
** The gradient eluent conditions are programmed in Chromeleon Wizard.

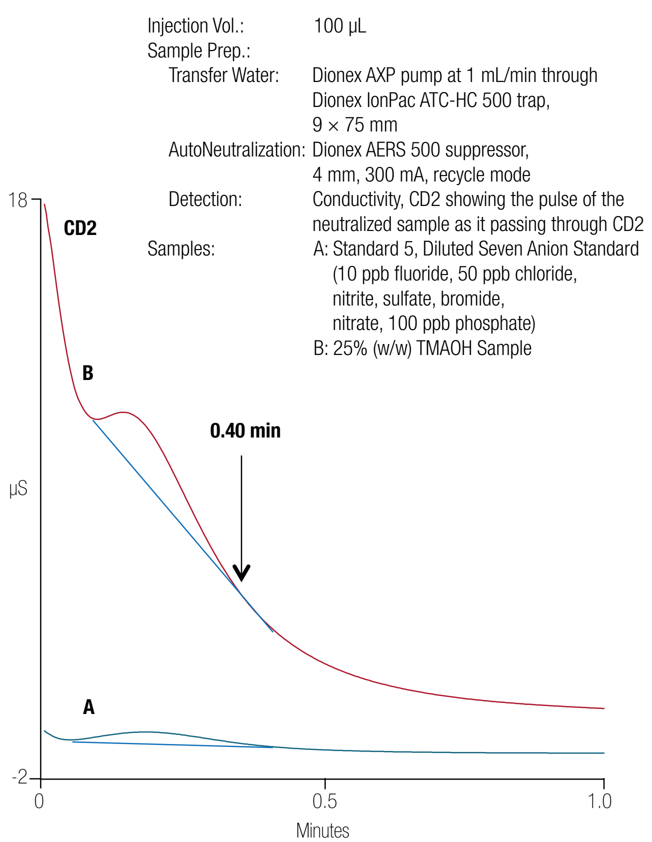

Figure 3. Experimentally determining the time needed (0.40 min) for AutoNeutralization by the CD2 conductivity response.

Results and discussion

AutoNeutralization

In the first step, the autosampler loads the base sample into the sample loop. Purified water delivered from the AXP pump and trap column (Dionex IonPac ATC-HC 500 trap column) is used to transfer the sample in the sample loop at 1 mL/min to the neutralizing suppressor and collected on the concentrator column. As the sample passes through the suppressor (4 mm high capacity Dionex AERS 500 Anion Electrolytically Regenerated Suppressor), the cation counter ion is exchanged with hydronium thereby neutralizing the base sample. Only a single pass through the suppressor is needed to neutralize the sample due to high neutralizing capacity. The trace anions are retained on the concentrator column while the water flows to waste, thereby also concentrating the trace anions of the sample.

Separation and detection

At the injection point, this portion of the method is a more traditional Reagent-Free IC (RFIC™) application. The trace anions elute from the concentrator column to the guard and separation columns. Here the trace anions are separated by an electrolytically generated hydroxide gradient at 0.25 mL/min on the Dionex IonPac AS18-4µm column. The Dionex IonPac AS18-4µm column was optimized for fast separations of inorganic anions, and is therefore an ideal choice for this application. This column is a high pressure column, 3,000 psi or higher, requiring a high-pressure capable IC system such as the Dionex ICS-5000+ HPIC or Dionex Integrion HPIC system. As the analyte peaks elute from the column, they are detected by suppressed conductivity detection using a 2 mm Dionex AERS 500 Anion Electrolytically Regenerated Suppressor and conductivity detector.

Figure 4 shows the typical separations and detection of seven inorganic anions in Standard 1 (0.2 µg/L fluoride, 1 µg/L of chloride, nitrite, bromide, sulfate, and nitrate and 2 µg/L phosphate). A water injection is shown for comparison. Although carbonate is the dominant peak, sulfate (Peak 8) is well resolved from carbonate. A carbonate removal device was not required to chromatographically resolve sulfate from carbonate as in the previous version of this application, thereby simplifying the application.

Method qualification

The Single Pass AutoNeutralization method was qualified by determining the linearity of the analyte responses to concentration, peak area and retention time reproducibilities, system blank cleanliness, the method detection limits (MDLs), and method accuracy.

Linearity and method detection limits

To determine the response relationship to concentration, the responses of triplicate injections of the six standards with DI water as Standard 0 were plotted against the analyte concentration using the calibration function. The results with $r^2 > 0.99$ are summarized in Table 5 indicating linear relationships for all seven anions.

Column: Dionex IonPac AG18-4µm, 2 × 30 mm
Dionex IonPac AS18-4µm, 2 × 150 mm
KOH Gradient: 23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min), 45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min), 23 mM (8.1–12 min)
Eluent Source: Dionex EGC-500 KOH cartridge, Dionex CR-ATC 500 trap column, Dionex high pressure degasser
Flow Rate: 0.25 mL/min
Injection Vol.: 100 µL
Column Temp.: 30 °C
Sample Prep.:
Transfer Water: Dionex AXP pump at 1 mL/min through Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization: Dionex AERS 500 suppressor, 4 mm, 300 mA, recycle mode, CD conductivity detector 2 for monitoring
Concentrator: Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.: 15 °C
Detection: Suppressed conductivity, Dionex AERS 500, 2 mm, 28 mA, recycle mode
Standards: A: DI Water
B: Diluted Seven Anion Standard 1 (0.2 ppb fluoride, 1 ppb chloride, nitrite, sulfate, bromide, nitrate, 2 ppb phosphate)
Peaks: 1. Fluoride 7. Bromide
2. Acetate 8. Sulfate
3. Formate 9. Nitrate
4. Chloride 10. System
5. Nitrite 11. Phosphate
6. Carbonate 12. System

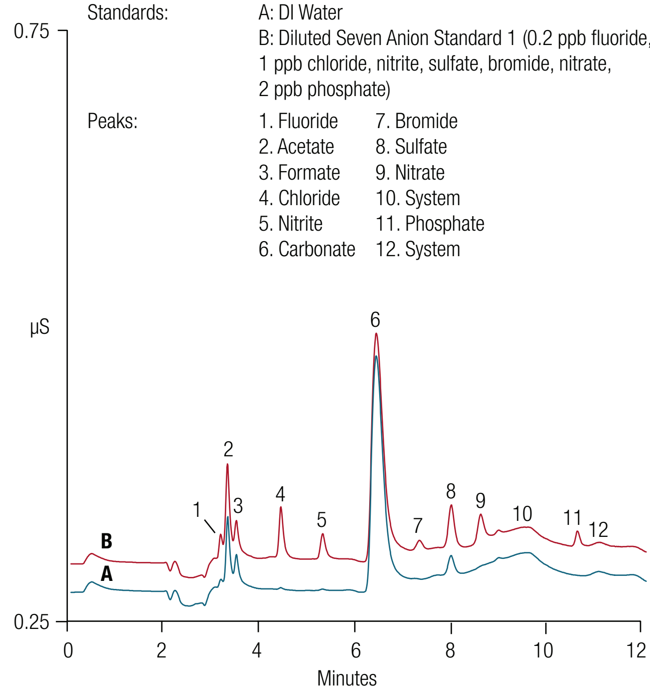

Figure 4. Trace Anions in DI Water and Seven Anion Standard using a single pass AutoNeutralization.

Table 5. Calculated coefficients of determination and method detection limits (MDLs).

	Linear Range (µg/L)*	Coefficient of Determination (r^2)	MDL** (µg/L)
Fluoride	0–10	0.9957	6.0***
Chloride	0–50	0.9999	0.34
Nitrite	0–50	0.9996	0.46
Sulfate	0–50	0.9996	8.7***
Bromide	0–50	0.9994	0.88
Nitrate	0–50	0.9999	0.92
Phosphate	0–100	0.9997	0.52

*DI water was used as Standard 0; linear with offset was selected for calibration.
**3.14 × average amount × %RSD/100
***3× system blank

Reproducibility

Figure 5 shows the reproducibility (n = 7) of the lowest concentration standard, Standard 1. The peak area reproducibilities were acceptable with RSDs from 0.9 to 3.3. Peaks 2 (acetate), 3 (formate), 6 (carbonate), and 10 (unknown) were not quantified.

The retention time reproducibilities (not shown) were determined by comparing single injections of each calibration standard. The results were acceptable, RSD < 1 % (fluoride: 0.55; chloride, 0.58, nitrite: 0.04; bromide: 0.98; sulfate: 0.41; nitrate, 0.09; phosphate: 0.50 %).

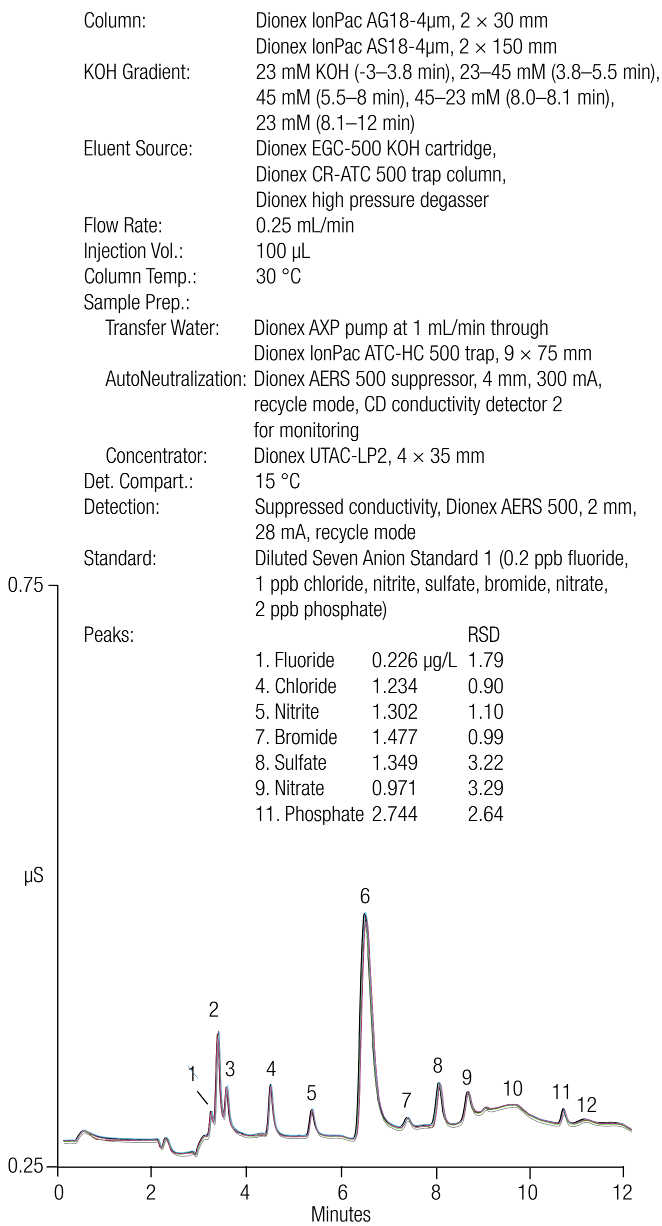

Figure 5. Reproducibility of seven injections of Anion Calibration Standard One.

System blanks

In all trace ion applications, the system and water blanks can often limit the detection limits of the analytical method and therefore are an important parameter when assessing the method qualification. Figure 6 compares a A) DI water injection, B and C) no-injection blank before and after injecting sodium hydroxide samples, D) transfer water blank (Dionex AXP Auxiliary Pump-purified DI water), and E) Standard 1. Sulfate and fluoride are detected in all blank samples, thereby limiting the detection limit to 3× the average contamination. Fluoride and sulfate contamination were more evident after analyzing the sodium hydroxide samples, implicating higher extractables from the hydroxide and implying that an additional pretreatment with hydroxide could reduce the contamination. Chloride was also detected at a low level, sub µg/L, in the transfer water and no-injection blanks. However as with most trace ion applications, lower ionic contamination can be achieved by continuing to run the system.

Method detection limits (MDLs)

MDLs were determined based on seven replicate injections of Standard 1, multiplying the mean concentration, the reproducibility (SD), and the Student *t*-test factor of 3.142. The calculated MDL results are summarized in Table 4. Each anion had a MDL < 1 µg/L with the exception of fluoride and sulfate. A standard MDL calculation method can not be used for these two anions because they were found in the system blanks (Figure 6). In these cases, the reported MDL is 3× the average concentration found in the blanks. MDLs will vary from lab to lab depending on water quality, lab environment, and the samples. However, it is notable that the hydroxide sample injection caused increased ionic contaminants to leach out into the following blank. Previously, a precleaning step with strong base has been effective in lowering MDLs for fluoride and sulfate in similarly strong base samples.[15] The simpliest approach is to load multiple hydroxide samples through the neutralizing suppressor while directing the flow out of the neutralizing suppressor to waste.

Column: Dionex IonPac AG18-4µm, 2 × 30 mm
Dionex IonPac AS18-4µm, 2 × 150 mm
KOH Gradient: 23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min),
45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min),
23 mM (8.1–12 min)
Eluent Source: Dionex EGC-500 KOH cartridge,
Dionex CR-ATC 500 trap column,
Dionex high pressure degasser
Flow Rate: 0.25 mL/min
Injection Vol.: 100 µL
Column Temp.: 30 °C
Sample Prep.:
Transfer Water: Dionex AXP pump at 1 mL/min through
Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization: Dionex AERS 500 suppressor, 4 mm, 300 mA,
recycle mode, CD conductivity detector 2
for monitoring
Concentrator: Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.: 15 °C
Detection: Suppressed conductivity, Dionex AERS 500, 2 mm,
28 mA, recycle mode
Samples: A: DI Water injection, D: Transfer DI water injection
B, C: No Injection Blank before and after hydroxide injections
E: Standard 1 (0.2 ppb fluoride, 1 ppb chloride, nitrite,
sulfate, bromide, nitrate, 2 ppb phosphate)—higher offset

Peaks:	A	B	C	D	E
1. Fluoride	0.24 µg/L	0.23	0.61 µg/L	2.0 µg/L	0.34 µg/L
2. Acetate	N.D.	N.D.	N.D.	N.D.	N.D.
3. Formate	N.D.	N.D.	N.D.	N.D.	N.D.
4. Chloride	–	–	0.24	0.24	1.2
5. Nitrite	N.D.	N.D.	N.D.	N.D.	N.D.
6. Carbonate	N.D.	N.D.	N.D.	N.D.	N.D.
7. Bromide	–	–	–	–	1.4
8. Sulfate	0.37	<0.2	2.9	2.8	1.3
9. Nitrate	N.D.	N.D.	N.D.	N.D.	N.D.
10. Unknown	–	–	–	–	–
11. Phosphate	–	–	–	–	2.8
12. Unknown	–	–	–	–	–

N.D. = not determined

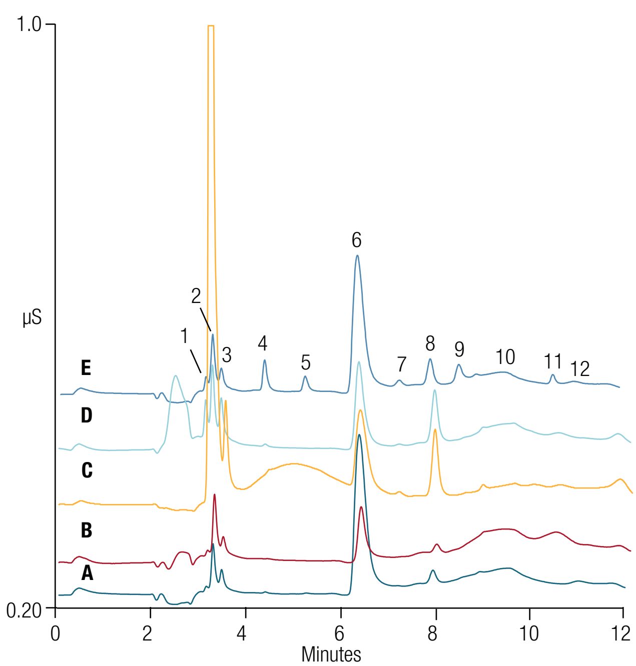

Figure 6. Comparison of trace anions in system blanks versus a Seven Anion Standard 1 injection.

Accuracy

Method accuracies were determined by averaging the measured concentration of triplicate injections of Standard 3 run as check standards after calibration. Table 6 shows good recoveries from the original standards, 87 to 107%.

The method qualification results demonstrate that the method is reproducible, accurate, has suitable blanks and detection limits, with the possible exceptions of sulfate and fluoride (depending on the detection limit requirements for the sample), and exhibits a linear relationship between response and concentration over the ranges tested for all seven analytes.

Sample analysis

The Single Pass AutoNeutralization method was applied to 25% (w/w) semiconductor grade tetramethylammonium hydroxide (TMAOH), 0.1 M reagent grade tetrabutylammonium hydroxide (TBAOH), and 5, 10, 25% (w/w) ACS grade sodium hydroxide (NaOH). The results are shown in Figures 7–10 and Table 7.

Figure 7 compares the trace anion concentrations found in the 25% TMAOH solution and the same sample with intermediate standard added to Standard 5 concentrations to confirm peak identification. To better assess accuracy, the sample can be spiked with a small amount of concentrated standard to generate a 0.5 to 3× increase in concentration of each analyte. Nitrate and nitrite were found to be unstable in this sample and all other base samples and therefore the concentrations and recoveries were not reported. Table 7 shows that the recovery results of anion concentrations added at Standard 5 levels, were 82–86%, within 80–120% recovery, except for 78% recovery of fluoride.

For the NaOH solutions (Figures 8 and 9), the neutralizing suppressor current was increased to 490 mA and the Dionex AXP Auxiliary Pump flow rate was reduced to 0.5 mL/min to increase the neutralizing efficiency and to increase the neutralizing time. Figure 7 compares the trace anions found in 5% (w/w) ACS grade NaOH before and after standard was added to Standard 5 concentration levels was added. The original 5% preparation solution contains significant

Table 6. Recovery results of Standard 3 as a check standard.

	Amount (µg/L)	Average Measured Amount (µg/L)	%RSD	Recovery (%)
Fluoride	2.0	1.74	0.88	87.1
Chloride	10.0	10.00	0.43	100
Nitrite	10.0	10.69	0.52	107
Bromide	10.0	9.79	0.68	97.9
Sulfate	10.0	10.68	1.38	107
Nitrate	10.0	8.80	1.02	88.0
Phosphate	20.0	19.93	1.29	99.6

n = 3

Table 7. Recovery results of samples.

	25% (w/w) TMAOH				5% (w/w) NaOH			
			Recovered				Recovered	
	Present (µg/L)	Added (µg/L)	(µg/L)	(%)	Present (µg/L)	Added (µg/L)	(µg/L)	(%)
Fluoride	2.1	10	9.5	78.5	1.5	10	8.9	77.4
Chloride	2.3	50	43.4	83.0	3470	50	N.D.	N.D.
Sulfate	7.3	50	49.5	86.4	896	50	N.D.	N.D.
Bromide	3.8	50	44.0	81.7	18.7	50	61.1	88.9
Phosphate	2.5	100	88.5	86.3	10.3	100	106.9	96.9

N.D. = Not determined

amounts of chloride and sulfate, > 800 µg/L. Because the concentrations were well outside the calibration range, recovery was calculated only for fluoride, bromide, and phosphate (Table 7). The results show low recovery for fluoride (79%) as a result of co-elution with acetate and formate and acceptable recoveries for bromide and phosphate – 88, and 96%, respectively.

Figure 9 compares the chromatograms of 5, 10, and 25% NaOH samples. Despite the high concentrations of anions in these samples, the results showed proportional increases when comparing 5% to 10% and 25% sodium hydroxide samples. Notice that the anion levels are well outside the calibration ranges and therefore the accuracy is not reliable without applying a sample dilution.

Figure 10 shows the trace anion determinations in ACS grade, 0.1 M TBAOH. The sample had high concentrations of bromide, phosphate and sulfate – 400 to 600 (µg/L) – and 23 (µg/L) of chloride.

In some samples, fluoride may co-elute with acetate and formate peaks making quantification difficult and resulting in low recovery and poor accuracy. When higher resolution of fluoride from acetate and formate is more important than fast separations, the Dionex IonPac AS28-4µm column is more suitable. The Dionex IonPac AS28-4µm column is optimized for higher resolving power of early eluters. Figure 11 demonstrates the determination of trace anions in DI water, a standard, and 0.1 M TBAOH using the Dionex IonPac AS28-4µm column and conditions. Fluoride is well resolved from acetate and formate, but with a cost of a longer run time, 25 min, for the complete anion separation. Additionally, this application is demonstrated using external water mode for both suppressors (delivered by a second AXP pump).

Column:	Dionex IonPac AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
KOH Gradient:	23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min), 45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min), 23 mM (8.1–12 min)
Eluent Source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 500 trap column, Dionex high pressure degasser
Flow Rate:	0.25 mL/min
Injection Vol.:	100 µL
Column Temp.:	30 °C
Sample Prep.:	
Transfer Water:	Dionex AXP pump at 1 mL/min through Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization:	Dionex AERS 500 suppressor, 4 mm, 300 mA, recycle mode, CD conductivity detector 2 for monitoring
Concentrator:	Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 2 mm, 28 mA, recycle mode
Samples:	A: Deionized water, B: 25% (w/w) TMAOH semiconductor grade, C: Sample B + 10 ppb fluoride, 50 ppb chloride, nitrite, sulfate, bromide, nitrate, 100 ppb phosphate

Peaks:	B	C		B	C
1. Fluoride	2.1	9.5 µg/L	7. Carbonate	N.D.	N.D.
2. Acetate	N.D.	N.D.	8. Bromide	3.8	44.0 µg/L
3. Formate	N.D.	N.D.	9. Sulfate	7.3	49.5
4. Chloride	2.3	43.4	10. Nitrate	N.D.	N.D.
5. Nitrite	N.D.	N.D.	11. Unknown	–	–
6. Unknown	–	–	12. Phosphate	2.5	88.5

N.D. = not determined

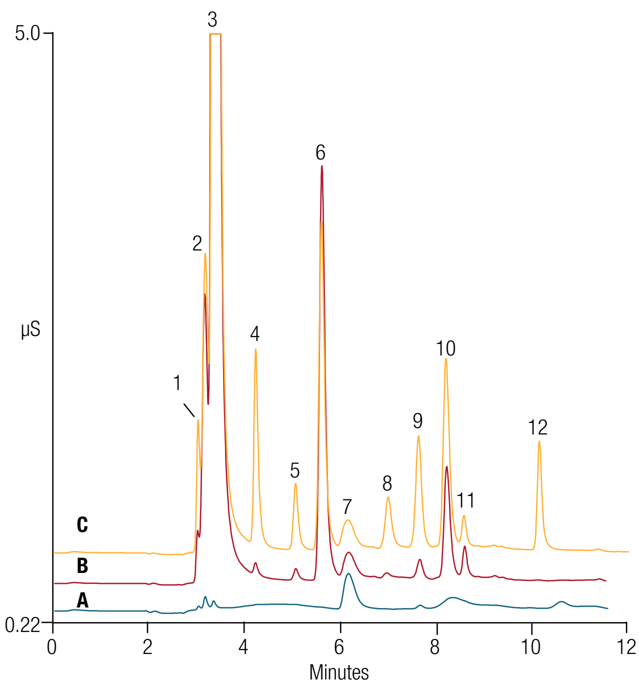

Figure 7. Trace Anions in a A) DI Water, B) 25% (w/w) semiconductor grade tetramethylammonium hydroxide (TMAOH) Solution, C) "B" spiked with Standard 5.

Column:	Dionex IonPac AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
KOH Gradient:	23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min), 45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min), 23 mM (8.1–12 min)
Eluent Source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 500 trap column, Dionex high pressure degasser
Flow Rate:	0.25 mL/min
Injection Vol.:	100 µL
Column Temp.:	30 °C
Sample Prep.:	
Transfer Water:	Dionex AXP pump at 0.5 mL/min through Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization:	Dionex AERS 500 suppressor, 4 mm, 490 mA, recycle mode, CD conductivity detector 2 for monitoring
Concentrator:	Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 2 mm, 28 mA, recycle mode
Samples:	A: Deionized water B: 5% (w/w) reagent grade sodium hydroxide solution C: Sample B + 10 ppb fluoride, 50 ppb chloride, nitrite, sulfate, bromide, nitrate, 100 ppb phosphate

Peaks:	B	C		B	C
1. Fluoride	1.4	8.9 µg/L	6. Carbonate	N.D.	N.D.
2. Acetate	N.D.	N.D.	7. Bromide	18.7	61.1 µg/L
3. Formate	N.D.	N.D.	8. Sulfate	896	N.D.
4. Chloride	3470	N.D.	9. Nitrate	N.D.	N.D.
5. Nitrite	N.D.	N.D.	10. Unknown	–	–
			11. Phosphate	10.3	107

N.D. = not determined

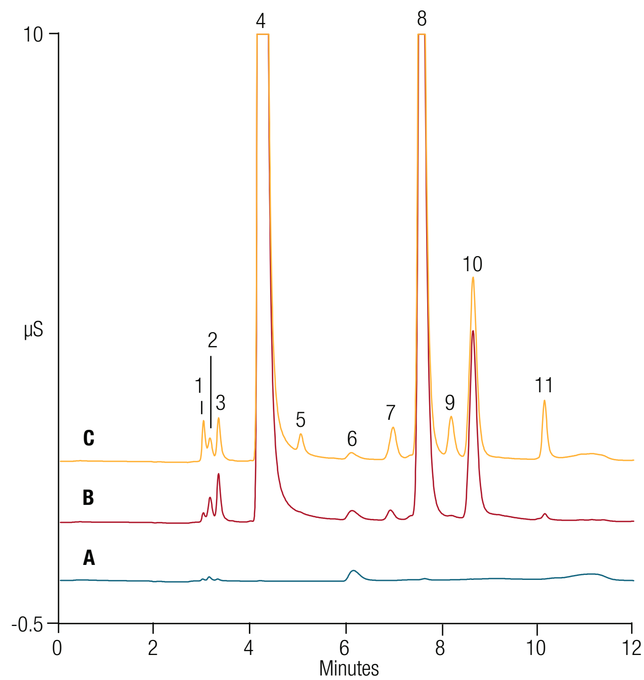

Figure 8. Trace anions in A) DI water, B) 5% (w/w) reagent grade sodium hydroxide solution C) "B" spiked with Standard 5.

Column:	Dionex IonPac AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
KOH Gradient:	23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min), 45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min), 23 mM (8.1–12 min)
Eluent Source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 500 trap column, Dionex high pressure degasser
Flow Rate:	0.25 mL/min
Injection Vol.:	100 µL
Column Temp.:	30 °C
Sample Prep.:	
Transfer Water:	Dionex AXP pump at 0.5 mL/min through Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization:	Dionex AERS 500 suppressor, 4 mm, 490 mA, recycle mode, CD conductivity detector 2 for monitoring
Concentrator:	Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 2 mm, 28 mA, recycle mode
Samples:	Sodium hydroxide A: 5% (w/w) B: 10% (w/w) C: 25% (w/w)

Peaks:	A	B	C
1. Fluoride	1.4 µg/L	3.2 µg/L	51.9 µg/L
2. Acetate	N.D.	N.D.	N.D.
3. Formate	N.D.	N.D.	N.D.
4. Chloride	3470	5880	10,800
5. Nitrite	N.D.	N.D.	N.D.
6. Carbonate	N.D.	N.D.	N.D.
7. Bromide	18.7	17.4	47.1
8. Sulfate	896	1640	N.D.
9. Nitrate	N.D.	N.D.	N.D.
10. Phosphate	10.3	16.3	94.5

N.D. = not determined

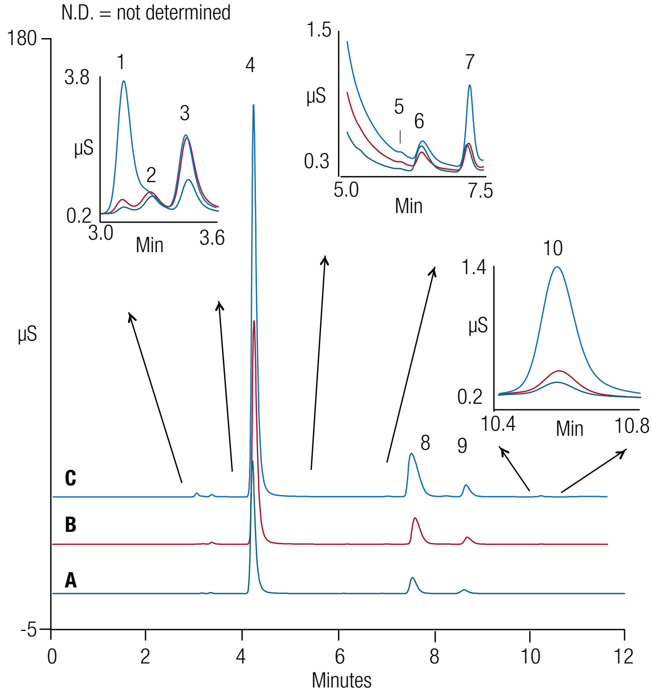

Figure 9. Trace anions in A) 5% (w/w), B) 10% (w/w), C) 25% (w/w) reagent grade sodium hydroxide solution.

Column:	Dionex IonPac AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
KOH Gradient:	23 mM KOH (-3–3.8 min), 23–45 mM (3.8–5.5 min), 45 mM (5.5–8 min), 45–23 mM (8.0–8.1 min), 23 mM (8.1–12 min)
Eluent Source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 500 trap column, Dionex high pressure degasser
Flow Rate:	0.25 mL/min
Injection Vol.:	100 µL
Column Temp.:	30 °C
Sample Prep.:	
Transfer Water:	Dionex AXP pump at 1 mL/min through Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization:	Dionex AERS 500 suppressor, 4 mm, 300 mA, recycle mode, CD conductivity detector 2 for monitoring
Concentrator:	Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 2 mm, 28 mA, recycle mode
Samples:	A: Deionized water B: 0.1 M TBAOH ACS grade

Peaks:	A	B	
1. Acetate	N.D	8. Bromide	564 µg/L
2. Formate	N.D.	9. Unknown	–
3. Chloride	23.1 µg/L	10. Sulfate	515
4. Unknown	–	11. Nitrate	N.D.
5. Unknown	–	12. Unknown	–
6. Unknown	–	13. Phosphate	354
7. Carbonate	N.D.	14. Unknown	–

N.D. = not determined

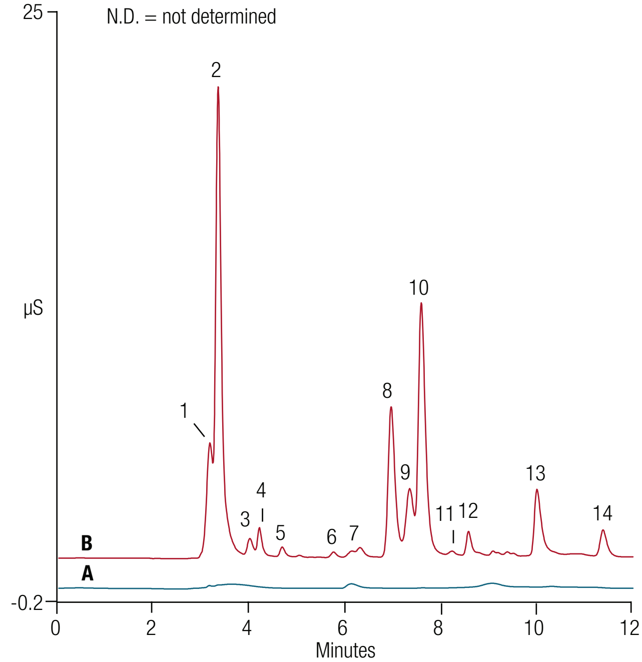

Figure 10. Trace anions in 0.1 M tetrabutylammonium hydroxide (TBAOH) ACS grade solution.

Column:	Dionex IonPac AG28-4µm, 2 × 30 mm Dionex IonPac AS28-4µm, 2 × 150 mm
KOH Gradient:	7 mM wash (-7 to 6 min), 7–20 mM (6–8 min), 20–72 mM (8–13 min), 72 mM (13–25 min), 7 mM (25 min)
Eluent Source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 500 trap column, Dionex high pressure degasser
Flow Rate:	0.3 mL/min
Injection Vol.:	100 µL by an AXP pump at 1 mL/min
Column Temp.:	30 °C
Sample Prep.:	
Transfer Water:	Dionex AXP pump at 1 mL/min with Dionex IonPac ATC-HC 500 trap, 9 × 75 mm
AutoNeutralization:	Dionex AERS 500 suppressor, 4 mm, 300 mA, external water by Dionex AXP pump at 1 mL/min
Concentrator:	Dionex UTAC-LP2, 4 × 35 mm
Det. Compart.:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 2 mm, 54 mA, recycle mode, Dionex CRD 200, 2 mm
Samples:	A: Deionized water blank B: Standard (1 µg/L fluoride, 5 µg/L chloride, nitrite, sulfate, bromide, nitrate, 10 µg/L phosphate) C: 0.1 M TBAOH reagent grade

Peaks:	B	C		B	C
1. Fluoride	1.2	2.2 µg/L	9. Carbonate	N.D.	N.D.
2. Acetate	–	–	10. Unknown	–	–
3. Organic Acid	–	–	11. Sulfate	5.1	557 µg/L
4. Formate	–	–	12. System	–	–
5. Unknown	–	–	13. Unknown	–	–
6. Unknown	–	–	14. Bromide	5.6	596
7. Chloride	5.4	29.3	15. Nitrate	N.D.	N.D.
8. Nitrite	N.D.	N.D.	16. Phosphate	10.5	98.2

N.D = not determined

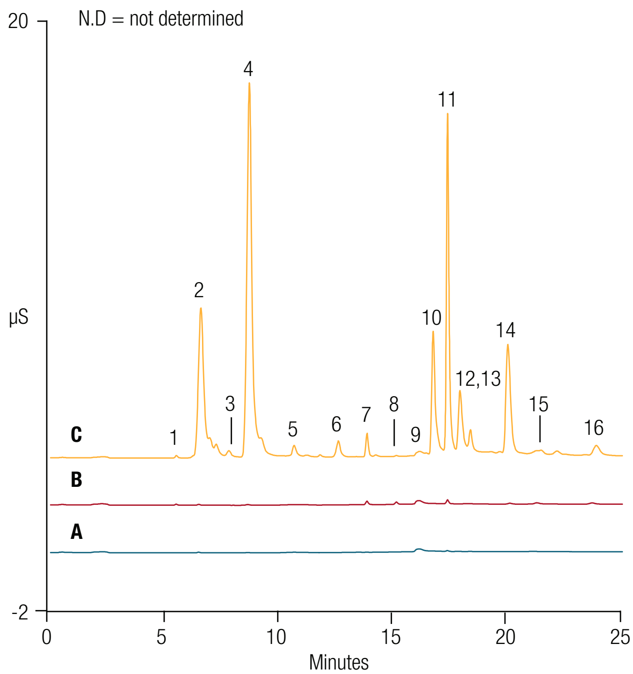

Figure 11. Trace anions in 0.1 M tetrabutylammonium hydroxide (TBAOH) ACS grade solution on IonPac AS28-4µm column.

Conclusion

Trace anions at ppb to ppm concentrations were determined in 100 µL of concentrated (molar to percent) amine and hydroxide reagent solutions using a Single Pass AutoNeutralization step to neutralize the sample. The neutralized sample was collected and concentrated onto a concentrator column, and finally analyzed by fast anion-exchange chromatography and suppressed conductivity detection. In this application, all seven inorganic anions were separated within 12 min using a Dionex IonPac AS18-4µm column, as compared to the 45 min in AN93 using Park and Neutralize. The method exhibited good precision and accuracy. This application was also demonstrated on Dionex IonPac AS28-4µm column which, unlike the Dionex IonPac AS18-4µm column, resolved fluoride from acetate and formate. However, to achieve that separation the sample run time was increased to 25 min.

This application is available in the Thermo Scientific AppsLab Library of Analytical Applications with an eWorkflow for the Dionex ICS-5000+ HPIC system.[16]

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