TECHNICAL NOTE 112

Determination of trace anions in ultrapure water using capillary ion chromatography

Authors
Terri Christison, Fei Pang, John Madden, Jim Schibler, Frank Hoefler, and Linda Lopez
Thermo Fisher Scientific, Sunnyvale, CA, USA

Keywords
Capillary ion chromatography, IC, trace, power, electronics, Dionex ICS-5000+, Dionex ICS-4000

Introduction

Trace anion determinations in ultrapure water (UPW) are important for the power and electronics industries. Ionic contamination at µg/L and ng/L concentrations can cause corrosion of important process equipment, resulting in accidents or costly unplanned maintenance. Additionally, ionic contamination in the electronics industry causes poor yields and early failures of important semiconductor and disk drive components.

Trace ion determinations have been thoroughly discussed in application documents published from 1996 to 2009.[1–7] However, detection limits, sample handling, and blank stability have all been improved by recent advances in ion chromatography (IC) technology, including Thermo Scientific™ Dionex™ IC systems, the Thermo Scientific™ Dionex™ AS-AP autosampler, and the Thermo Scientific™ Dionex™ ICW-3000 Online Water Purifier:

- Capillary IC separates ions on 0.4 mm diameter columns at 10–30 µL/min flow rates, which increases mass sensitivity, reduces water consumption, and reduces waste generation to only ~5 L/year. The increased mass sensitivity is ideal for trace analysis, but also presents new challenges in preventing contamination from the lab environment. Now smaller sample volumes—from 25 to 100 times less than those used on microbore or standard bore systems, respectively—can produce the same results.

- The Dionex AS-AP autosampler is the injector of choice for capillary IC. It can inject very small volumes for sample-limited scenarios, but it can also load samples from 10 mL vials directly onto a concentrator column without a separate sampling pump. This reduces system cost and complexity, and also eliminates a potential source of contamination. For low ng/L ion determinations, the sample should be introduced by a pneumatic sample delivery accessory.
- The ICW-3000 supplies ultrapure water directly to the capillary IC system, eliminating many contamination risks and helping to provide consistently low blank levels.

This document discusses the application of these technologies to trace-level analysis, and provides specific guidance for laboratory techniques that are essential for achieving good results when performing ultratrace analyses.

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-5000 capillary IC system* consisting of:
  - Thermo Scientific™ Dionex™ SP Single Pump or DP Dual Pump capillary module
  - Thermo Scientific™ Dionex™ EG Eluent Generator module
    - Capillary EGC cartridge; Anions: Thermo Scientific™ Dionex™ EGC-KOH (P/N 072076)
    - Thermo Scientific™ Dionex™ Capillary Continuously-Regenerating Anion Trap Column: Thermo Scientific™ Dionex™ CR-ATC (P/N 072078)

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system or the Thermo Scientific™ Dionex™ ICS-4000 Capillary HPIC™ system.

- DC Detector/Chromatography module
  - Thermo Scientific™ Dionex™ Capillary CD conductivity detector (P/N 072041)
  - Thermo Scientific™ Dionex™ IC Cube™ capillary module (P/N 072000)
    - Degas cartridge (P/N AAA-074459)
    - Capillary column tray
    - Capillary Electrolytic Suppressor (CES), Anions: Thermo Scientific™ Dionex™ ACES™ 300 (P/N 072052)
    - Anions: Thermo Scientific™ Dionex™ CRD 200 Carbonate Removal Device (P/N 072054)
  - High-Pressure Valve Pod, 6-port (P/N 061947)
- Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 074921 or 074926)
- Thermo Scientific™ Dionex™ ICW-3000 Inline Water Purifier (P/N 075386) as the water source for eluent, AS-AP autosampler flush water, and suppressor regenerant
- Concentrator Columns: Thermo Scientific™ Dionex™ IonSwift™ MAC-100 (P/N 063889) for determinations
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS)
- Thermo Scientific™ Dionex™ Vial Kit, 10 mL Polystyrene with Caps and Blue Septa (P/N 074228); for ultratrace work, PTFE single injection septum (P/N 074927)
- Corning® polystyrene non-treated culture flasks (Fisher Scientific, P/N 08-757-502) for low-level standards and samples
- Gloves, Ansell Nitrilite®, nitrile cleanroom Class 5 (Fisher Scientific, P/N 19-014)
- Berkshire® Gamma Wipe® 120 cleanroom wipes, polyester (Berkshire, P/N GW120ST15; Fisher Scientific, P/N18-999-306)
- Thermo Scientific™ Nalgene™ filter flask containers for soaking vials, caps, septa, pipette tips, or connectors (P/N 164-0020)

Reagents

- Thermo Scientific™ Dionex™ IC Standards
  - 1,000 mg/L Fluoride (P/N 037158)
  - 1,000 mg/L Chloride (P/N 037159)
  - 1,000 mg/L Sulfate (P/N 037160)
  - Combined Seven Anion Standard II (P/N 057590)
- SPEX CertiPrep® (Fisher Scientific, P/N AS-NO29, AS-NO39, AS-PO49, AS-CL9, AS-SO49, AS-BR9, AS-F9) or UltraScientific certified IC Standards (Fisher Scientific, P/N USICC001, USICC002, USICC003, USICC004, USICC005, USICC006. USICC007)

Preparing for successful trace level (<10 µg/L) and ultratrace (< 500 ng/L) ion determinations

There are many sources of contamination that can interfere with reliable and consistent trace ion determinations. Working in a trace analysis environment requires patience, consistent work routines, and awareness of normal lab activities and items that pose contamination risks. This section discusses and reviews the importance of clean water; an isolated clean, low-particle work environment; the selection and use of laboratory gloves; the effects of behaviors, social interactions, personal care products; and tools suitable for the trace analysis work area.

1. Water: A reliable, point-of-use source of freshly generated 18.2 MΩ·cm deionized (DI) water is essential for trace ion determinations. Proper use of the water purification system is also important.

   a. Use only a recirculating point-of-use DI dispenser/deionizer with a resistivity display.

   b. Use the DI water from the point-of-use system only after the water has been flowing for > 1 min and displays 18.2 MΩ·cm resistivity.

   c. Allow the DI water to flow continuously when dispensing for standard/sample preparation.

   d. Install the Dionex ICW-3000 Online Water Purification system to provide pure DI water directly to the eluent pump, Dionex AS-AP autosampler syringe, and CES suppressor regenerant, thereby eliminating contamination from the environment and the extractables from the eluent and autosampler containers. (The installation is discussed in the Setup section.)

2. Work environment: Airborne particles can contaminate your trace work area. To minimize airborne contamination:

   a. Isolate the instrument in a low-traffic area away from heater, air conditioner, and instrument vents, and away from chemical storage and weighing areas.

   b. Wipe down all surfaces using cleanroom wipes and fresh DI water.

   c. Minimize group discussions near the work area. People can stir up and emit dust particles and aerosols of ionic contamination.

   d. If available, use a laminar flow hood or a Class 10 cleanroom environment.

3. Gloves: Gloves can be a significant source of contamination to the sample, blank, and standard solutions. The gloves listed below are some of the cleanest available.

   a. Use powder-free Class 10 or Class 100 undyed nitrile cleanroom gloves (such as Ansell Nitrilite®, Fisher Scientific, P/N 19-014-687, 19-014-688, 19-014-689)

   b. Touch only the glove sleeves when putting on gloves. Never touch the glove tips.

   c. Select the glove size that results in a comfortable but tight fit. The glove tips should not extend past your fingers more than a few millimeters. Oversize gloves can easily contaminate the sample containers.

   d. Always wear gloves in the trace analysis work area.

e. Discard the gloves after touching your face, hair, or extra surfaces, especially any concentrated standards, solid reagents, or paper products.

f. Avoid touching the neck or cap of the sample container or standard container.

g. Never allow the gloves to touch the water or water from the gloves to drip or splash into soaking containers, sample, or standard solutions.

4. Personal: Personal care products such as deodorant, powders, hair products, makeup, perfume, and lotions can contribute contamination.

a. These items are not allowed in a Class 100 or better cleanroom environment because of the contamination they can cause.

b. In a non-cleanroom environment, these items should be considered as potential contamination sources. Analysts should minimize personal product use, especially during the initial development of the trace analysis method to minimize time spent on eliminating contamination sources.

c. Talking, sneezing, laughing, and coughing generate airborne mists of particles containing high concentrations of sodium, ammonium, potassium, chloride, sulfate, and organic acids. Note that one grain of salt in a cup of water is equivalent to ~20 mg/L chloride.

1) Avoid touching your face, hair, and skin when preparing any samples or rinsing.

2) Wear a cleanroom mask when preparing samples and standards.

3) Discard any solution and re-clean containers exposed to sneezing or coughing.

4) Refrain from eating or handling high-salt foods (such as snack foods and sauces) during work hours. These items have typically g/L concentrations of salt.

5) Discourage groups of people from gathering and talking in the trace analysis area because of they can increase environmental contamination, especially for ammonium, organic acids, sodium, potassium, and chloride.

5. Tools: Do not share tools. Isolate tools used in the trace analysis area to prevent contamination.

a. Cellulose products: Any type of cellulose products—including lab wipes, weighing paper, and cotton swabs contain high concentrations of chloride and sulfate and therefore are major sources of contamination.

1) Use low-particle, low ionic contamination polyester wipes, such as Berkshire Gamma Wipe 120 Class 10 cleanroom wipes.

b. Adhesives, tape, labels, and markers: Adhesive-backed paper and vinyl labels have high concentrations of chloride and sulfate.

1) Avoid using adhesive-backed vinyl or paper labels and tape.

2) Use either cleanroom adhesive tape or labels, or use markers to label samples.

c. Plastics and elastomers:

1) Do not use plastic weighing dishes to handle anything related to standards and samples; instead, tare final containers, and transfer materials directly from their source to final containers.

2) Use only polystyrene or FEP (Fluorinated ethylene propylene polymer) for containers and only polystyrene for vials.

3) Use only septa that have been verified to be contaminant-free, such as blue septa or (preferably) single-use PTFE septa. Conventional red septa have been found to release particles that can become lodged in the capillary system and become a source of ongoing contamination.

d. Pipettes: Most pipettes and pipette tips are not suitable for trace analysis.

1) Use pipette tips only when preparing concentrated standards, such as the intermediate standard, and not for any low-level work. Use only verified clean pipette tips, such as Rainin® boxed pipette tips.

2) Before using pipette tips, soak them in fresh deionized water in a pre-cleaned polystyrene flask, and handle them only with stainless steel alloy (SS 416) tweezers to further ensure cleanliness.

e. Glass: Glass containers are unsuitable for ion determinations.

f. Tweezers: Tweezers are a critical tool for handling pre-cleaned septa.

1) Select a pair of SS 416 tweezers to handle vial septa.

2) Isolate this pair of tweezers in the trace analysis area.

3) Never touch the septa with hands or gloves. Discard any septa that fall in the sink or on the floor.

4) Always rinse the tweezers prior to use and never allow the tips to touch the bench or other contaminated surface.

g. Wash bottles: Wash bottles are not recommended for use in trace ion analysis because they are considered a hidden contamination source. Contaminants have been found in wash bottles at levels as high as mg/L. If risking using a wash bottle:

1) Never use a wash bottle used by other lab chemists.

2) Never use a wash bottle to top-off standard and sample solutions.

3) Select a wash bottle made of FEP.

a. Isolate and dedicate an FEP squirt bottle for trace analysis.

b. Rinse and fill the bottle just prior to use, or at least daily, with freshly generated DI water.

h. Reagents and concentrated standards: Small amounts of reagents and concentrated standards can easily contaminate water blanks, the system, and other samples.

1) Avoid cross-contamination by isolating trace containers from those with higher concentrations.

2) Avoid close proximity to reagents, concentrated standards, and balances.

i. Soaps and detergents: Soaps and detergents typically contain high concentrations of sodium, sulfate, and calcium. Additionally, soaps and detergents are difficult to remove because their surface tension is lower than water.

1) Never use any soaps or detergents on any containers intended for samples, standards, or anything introduced into the IC system.

Standard and sample preparation

For successful trace ion determinations, it is crucial to minimize contamination to the sample and standard containers. This section is intended to be most helpful during the starting phases or the troubleshooting of a trace analysis method. Here are some of the general practices, followed by sections discussing the preparation of containers and standards, and a brief statement about collecting samples.

Preparing containers

Preparing samples and standards for trace analysis requires containers that have low extractable ionic contamination, and special handling techniques. Two types of containers have low ionic contamination suitable for trace analysis: non-treated polystyrene culture flasks and FEP containers. Non-treated polystyrene (Corning) culture flasks are recommended for storing samples and standards. Never use caps with liners or filters because the liners and filters typically contain mg/L concentrations of chloride and sulfate. FEP low particle (Eagle Picher, P/N B664) containers are also suitable for trace analysis but are more costly.

To prepare (clean) the flasks, turn on the 18.2 MΩ·cm DI water, rinse the flask five times with 18.2 MΩ·cm DI water, fill the flask to the top (leaving as little air as possible), cap it with a cap that has been pre-rinsed five times, and let soak overnight. Repeat the same rinsing and soaking process daily for at least 3 days. Use marking pens to label containers. Although marking pens can also leave residual ionic contamination, the contamination is significantly lower than what can be potentially introduced by adhesive-backed paper and vinyl labels.

Stock standards

To minimize contamination, use only certified prepared IC stock standards (SPEX CertiPrep, Ultra Scientific or Thermo Scientific Dionex brand standards).

Preparing 100 µg/L intermediate mixed anion standard

To prepare the mixed intermediate anion standard, turn on and leave on the DI water faucet until the standard is prepared. Follow the same rinsing process on the pre-cleaned flask by rinsing it five times with DI water. Shake out the excess water, and tare the flask on a top-loading balance. Fill the flask directly from the DI water faucet with DI water to ~250 ± 1 g. If the water weight is < 249 g, quickly tip the flask under the faucet. If the flask contains > 251 g, gently flick the excess water into the sink. (Turn off the DI water.) Record the weight. Using a Rainin pipette with a disposable pipette tip, transfer 25 µL each of the certified 1,000 mg/L fluoride, chloride, nitrite, sulfate, bromide, and nitrate standards into the flask containing the previously weighed DI water. Record the final weight, cap, gently mix, and recalculate the actual concentrations based on the volume of standard in the total weight. The approximate concentrations for each anion are ~100 µg/L. This flask should only be used for this standard because it can introduce contamination in lower concentration samples and standards. Therefore this flask should never be used to store samples or working standards unless the container is re-cleaned and verified clean by testing to < 10 ng/L ion concentrations.

Preparing the working standards

To prepare the working standards, for example a 1 µg/L mixed anion standard, turn on and leave on the DI water until the preparation of the standard is complete. Rinse the pre-cleaned flask five times, shake out the excess water, tare the flask on the top-loading balance, and fill the flask directly with the running water to ~246.5 ± 1 g. Do not use a transfer container because this is another potential contamination source. If the water weight is < 245 g, quickly tip the flask under the faucet. If the flask contains > 247 g, gently flick the excess water from the flask into the sink. Record the weight. Pour ~ 2.5 ± 0.5 g of the 100 µg/L intermediate anion standard into the flask carefully and slowly. Record the actual weight, cap, gently shake, and recalculate the concentrations. (Turn off the DI water.) Prepare a 100 ng/L working standard in a similar way, by pouring 25 ± 0.5 g of the 1 µg/L into a pre-cleaned flask containing 225 ± 1 g of DI water.

Collecting samples

Sample collection procedures are typically defined by the specific industry. However, all industries requiring trace analysis have the same general need to reliably collect samples that are representative of their process, in clean containers without cross-contamination. Here are some brief guidelines:

1. Collect samples in pre-cleaned and tested clean containers, described in the Preparing Containers section.

2. If possible, allow the liquid from the sample port to run for 1 min prior to collecting the sample to prevent sampling that does not represent the process. Sampling ports are backwash areas and can also collect sediment separated from the main process container.

3. To minimize environmental contamination to the sample, collect the sample as close to the sample port as possible without touching the port.

4. Immediately cap the container with a pre-cleaned (filter-less and liner-less) cap.

5. Label as appropriate, preferably with a marker.

Preparing the system

Use only precision-cut tubing on the capillary IC system, and on the Dionex AS-AP autosampler.

Connectors and ferrules

To minimize contamination from the connectors and ferrules, use only new parts and soak them in pre-cleaned polystyrene flasks containing fresh 18.2 MΩ·cm DI water.

Installing the Dionex ICW-3000 Online Water Purifier System

The Dionex ICW-3000 Online Water Purifier is critical to achieving trace ion determinations, especially as the analytical range approaches ng/L. To install the Dionex ICW-3000 Online Water Purifier:

1. Follow the Setup and install the Dionex ICW-3000 system according to the Dionex ICW-3000 installation instructions.[8]

2. Install the IC connections according to Figure 1. Assemble the fittings connecting to the eluent pump and the autosampler syringe as shown in Figures 2–3.

3. Direct the IC connections to waste and recirculate the Dionex ICW-3000 overnight.

4. Install the electrical connections and the IC connections according to the Dionex installation instructions.[8]

5. Configure the software control according to the Dionex installation instructions.

6. Replace the Dionex ICW-3000 water purifier tank with fresh deionized water regularly to minimize microbiological contamination.

For more information see TN 115.[9]

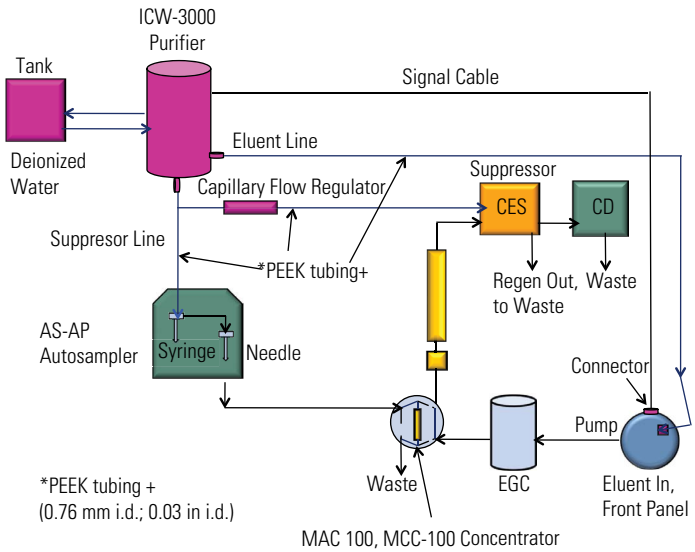

Figure 1. Configuring the Dionex ICW-3000 to the Dionex Capillary ICS-5000 IC System

Figure 2. Flat ferrule.

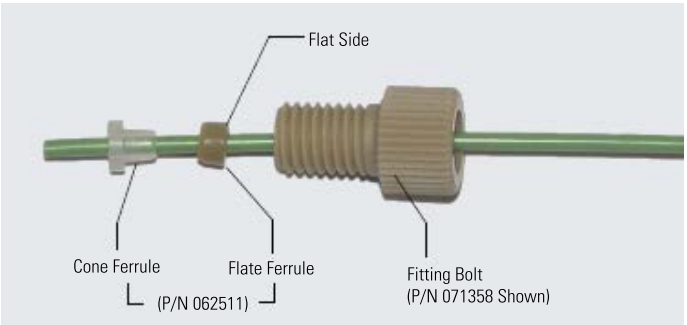

Figure 3. Assembly of ferrules.

Preparing the Dionex AS-AP Autosampler for trace ion analysis

As with all autosamplers, it is critical that the flow path be free of air bubbles to attain good chromatography and performance. Flush the flow path from the Dionex ICW-3000 Online Water Purifier to the syringe and sampling needle, and from the transfer lines to the diverter valve and injection valve. Align the autosampler needle to the sample tray and the autosampler injection port, and autosampler wash port, and calibrate the sample transfer lines (TLV) from the sampling needle to the injection port according to the Dionex AS-AP Operator's manual.[10]

The Dionex AS-AP Autosampler has many features that improve sample introduction for trace analysis applications. However, additional steps are needed to ensure that accessories do not contaminate the system. Additionally, the configurations are discussed for both direct large loop injections and large volume injections by concentration.

1. Tubing:

   a. Replace any Teflon tubing, such as in the buffer loop or wash reservoir line, with new green PEEK™ tubing.

   b. If the autosampler has been previously used to inject samples from vials other than polystyrene vials or polystyrene vials with red septa:

      1) Replace the PEEK tubing from the sampling needle to the injection port with new PEEK tubing.

      2) If the diverter valve is used, replace the PEEK tubing from the sampling needle to the diverter valve and from the diverter valve to the injection port.

2. Configuration for Large Loop and Concentrate Mode Injections:

   a. Plumb the Dionex AS-AP autosampler in push mode or in push sequential mode according to the Operator's Manual.[10]

   b. Add the autosampler to the instrument configuration in the Chromeleon software, as described in the product manual, *Configuring the AS-AP in Chromeleon.*

   c. Follow the instructions on the *General, Sharing,* and *Segments/Link* pages in the Operator's Manual.

      1) Enter the tray types on *Segments/Lin*k page.

      2) Select *none* for Pump links.

      3) Select *none* for Monitor links. (The pH/conductivity functions are activated through the Monitor links. However, these functions are not compatible with low ionic strength samples typically found in trace ion analysis.)

   d. The *Options* page

      4) Select injection mode as either push or sequential push in the drop down options.

      5) If the diverter valve is being used, select diverter valve in drop down options for the diverter valve (top or bottom).

      6) Select 1,200 µL for the buffer loop size and 250 µL for the syringe size.

      7) For the loop size, enter the actual loop volume for a normal capillary or a large loop injection. Enter the sample volume to concentrate for concentrate mode. Save the configuration file.

3. *Needle Alignment* and Transfer Line Calibration:

   a. Align the needle according to the Operator's manual and the instructions under Needle Alignment on the Chromeleon Autosampler panel.

   b. Prime the autosampler flush lines with 1,000 µL. Calibrate the transfer lines according to *TLV Calibration* instructions on the Chromeleon Autosampler panel.

4. Specific for Large Loop Injections Using the Dionex AS-AP Autosampler:

   a. Instrument configuration: On the Options page for the Dionex AS-AP autosampler, enter the loop volume into the Loop Size field.

   b. Instrument Method/Instrument Program Wizard: On the Sampler Options page.

      1) Select *PushSequentialFull* or *PushFull* in the I*nject Mode* field.

2) If a diverter valve is being used, select position 1 or 2 on the *Diverter Valve Position* boxes.

3) Enter 10.0 for the *Loop Overfill* field.

c. Instrument Method/Instrument Program Wizard: On the second *Sampler Options* page.

1) Enter 500.0 in the *Wash Volume* field.

2) Select *Both* for Injection Wash Mode field.

3) Use the recommended values for the remaining fields.

5. Specific for Concentrate Mode injections using the Dionex AS-AP autosampler: To achieve the highest reproducibility when concentrating a large volume, program the autosampler as if it were a partial loop injection of a very large volume. The sample must be delivered at low syringe speeds needed for the capillary concentrator column to efficiently retain the anions.

a. Server Configuration program: Program the autosampler as if it is a partial loop injection onto the concentration column. Enter a large volume, such as 800 µL, rather than the volume to be concentrated.

b. Instrument Method Wizard or Program Wizard:

1) Select *PushSeqPartial* or *PushPartial* in the Inject Mode field.

2) Enter 2.0 (µL/s) for the Draw and Dispense speeds (syringe)

3) Select Both for the Injection Wash Mode field

4) Enter 100 (µL) for Cut Volume field. Loop Wash factor should be unavailable.

5) Use the recommended values for the remaining fields

c: Sequence: Enter the sample volume to be concentrated.

6. Cleanup:

a. Soak the PEEK needle overnight in a previously cleaned vial or culture flask filled with fresh DI water. After installing the needle, re-check the alignment.

b. Repeatedly Flush and Prime the syringe, needle, and buffer loop with 12,000 µL DI water. It is important to keep the buffer loop clean.

c. If a diverter valve is used, flush DI water through both positions.

d. Ensure that the needle assembly is properly drained, so that no standing water can accumulate around it.

7. Vials, Caps, and Septa:

a. Use only the 10 mL polystyrene vials with either the blue septa or the single injection PTFE septa for trace analysis. The single injection PTFE septa are preferred over the blue septa.

b. Always handle the vials by the middle or bottom. Never touch the vial threads.

c. Always handle the septa with SS 416 tweezers. Discard any septa that fall in the sink or on the floor.

d. Always wear nitrile cleanroom gloves.

e. To ensure cleanliness suitable for trace analysis, rinse the vials, caps, and septa five times under running DI water, and then soak them in a pre-cleaned polystyrene container for 2–3 days.

f. After cleaning the vials, caps, and septa, decant the water, rinse the trace analysis SS 416 tweezers, remove a cap with the tweezers, and rinse the cap under running DI water. Shake the cap to dislodge any water. Transfer the cap to the other hand, without touching the edge of the cap.

g. Rinse the tweezers under running DI water, remove a blue or PTFE septum with the SS 416 tweezers, rinse the septum under running DI water, shake off the excess, and place the septum itnto the previously cleaned cap. Place the cap on the cleaning container.

h. Remove a vial without touching any remaining water in the container. Rinse the vial five times under running water, shake off the excess, add the sample, and secure the cap and septum.

Trace analysis using a capillary IC system

The Dionex ICS-5000 capillary IC system provides increased mass sensitivity, so it can achieve the same results as conventional-scale systems using smaller sample volumes. For example, injection or preconcentration of 100 µL sample on a capillary system is equivalent to a 10 mL sample on a standard 4 mm system. This increased mass sensitivity also reveals lower amounts of environmental contaminants and thus requires extra diligence in trace analysis. Additionally, the low flow rates require extra attention to reduce void volume and flush air from the system.

To achieve good chromatography by capillary IC, it is critical to:

- Use precision-cut tubing, blue connectors, and blue ferrules for all connections
- Make void-free plumbing connections between the tubing and the connection
- Hydrate and install all the cartridges in the Dionex IC Cube according to the Dionex ICS-5000 Operator's manual
- Diligently remove air from the system initially and after any change to the system, including stopping the pump. The pump is designed to ramp the pump speed to prevent pressure surges. This is a useful function but it can interfere with attempts to stabilize the flow rate. To override this function, enter the desired flow rate, then turn the pump on, off, and on again.

This section reviews the basic installation and critical trace analysis techniques to emphasize the importance of these techniques. For thorough, step-by-step instructions on installing the consumables in the Dionex ICS-5000 capillary IC, including the columns, refer to the Dionex ICS-5000 Installation and Operator's manuals, and TN 112 and 113.[10–13]

Installing a 6-port pod for large loop and concentrate mode injections

A 6-port injection valve is needed to inject sample volumes > 0.4 µL and to concentrate large sample volumes onto a concentrator column. Typically, this configuration for an Dionex ICS-5000 capillary system is installed at the factory. However, this configuration can be installed on the capillary system as needed. To replace the 4-port valve pod with a 6-port valve pod, follow the instructions in the Dionex ICS-5000 Operator's Manual:

Fittings and tubing

Precision-cut tubing, and proper installation of tubing and fittings are critical to achieving good chromatography. Additionally, cleaning the connectors and ferrules is necessary to minimize contamination introduced into the system.

1. Use only blue colored ferrules and connectors which are designed for the capillary IC system. To minimize contamination, soak the ferrules and connectors in a pre-cleaned polystyrene container.

2. Use only blue precision-cut tubing provided in the capillary IC kits. If possible, use precision-cut tubing for the sample loop. The precision cut ensures that the tubing end is flat, which minimizes the void between the tubing and connector.

3. To achieve good chromatography performance in the capillary IC format, it is critical to plumb the system without voids at any of the connections, as described in the Dionex ICS-5000 Installation Manual:

   a. For example, to install the blue precision-cut tubing from the capillary pump mixer to the capillary Dionex EGC cartridge and then the capillary Dionex CR-ATC column, first turn the pump on and wait until liquid is flowing steadily out of the tubing.

   b. Push a connector and a ferrule onto the tubing with 2 mm or more of tubing extended beyond the ferrule (Figure 4). (To ensure a good connection, you can extend the tubing 5 mm beyond the ferrule.)

   c. Place the tube into the inlet port of the capillary Dionex EGC cartridge. While holding the tube firmly in contact with the inlet port, screw in the connector as tight as you can using your fingers. Then tighten an additional ¾ turn with a wrench.

d. Wait until liquid has filled the outlet port and is flowing out of the capillary Dionex EGC cartridge, and then connect the next piece of tubing in the same manner.

e. Apply this process during plumbing of all tubing connections and after restarting the pump for any reason. It is critical to be diligent to prevent air from getting into the system.

f. To minimize introduced air after the pump has stopped, disconnect the connection from the degas cartridge to the injection valve, turn on the pump and repeat the instructions for proper connections to all of the connections sequentially to the final connection from the capillary Dionex CD detector to the regeneration tubing of the suppressor. This careful attention to the flow path minimizes the inadvertent introduction of bubbles which results in poor chromatography".

g. If the retention time reproducibility is poor, air bubbles may be caught in the injection valve. To flush the bubbles from the valve, temporarily increase the flow rate to 15 – 20 µL/min.

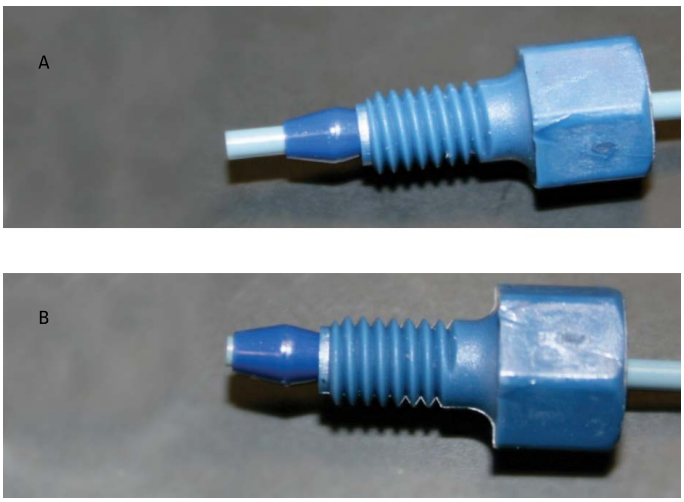

Figure 4. A) Correct. B) Incorrect.

Capillary carbonate removal device, Dionex CRD 200 cartridge

In trace anion analysis, the carbonate peak from the sample is always very large and can interfere with quantification of some the analyte peaks. Therefore a Carbonate Removal Device, Dionex CRD 200 cartridge, must be installed and plumbed inline.

Separation and concentrator columns

Select columns recommended for trace analysis, such as Dionex IonPac AS15, AS17C and AS25 capillary columns, and Dionex IonSwift MAC-100 monolith concentrator columns.

General system cleanup

Special system cleanup is typically needed for trace ion analysis. Typically, the injection valve, diverter valve, PEEK needle, and the tubing may require additional cleaning. Replace the Dionex ICW-3000 water purifier tank with fresh deionized water every month to minimize microbiological contamination.

1. After replacing the Dionex ICW-3000 water purifier tank, prime and restart the pump. To minimize introduced air, disconnect the connection from the degas cartridge to the injection valve, and repeat the instructions for proper connections.

2. For large loop injections, install the intended sample loop as instructed in the Large Loop Injection section. For concentrate mode injections, temporarily install a known clean 10–100 µL sample loop.

3. Bypass the analytical column by connecting the inlet of the suppressor directly to the outlet of the injection valve.

4. To clean the system, set the flow rate to 20–30 µL/min, the eluent concentration to 100 mM, and the suppressor current to 35 mA, then monitor the baseline for 2–3 hr. Toggle the injection valve between the load and inject positions every 15–30 min. Continue this process until both positions give a baseline conductivity of < 0.7 µS.

5. Stop the pump, disconnect the degas cartridge outlet from the injection valve, turn-on the pump and sequentially loosen and reconnect fittings in the flow path, following the instructions for proper connections given in the Fittings and Tubing section. This careful attention to the flow path minimizes the inadvertent introduction of bubbles which results in poor chromatography.

Direct large loop injections

For successful large-loop injections, the system must be kept very clean, and the sample loop must be installed without any voids between the tubing and port. This section briefly reviews the installation of the sample loop, and summarizes the important software settings in the instrument configuration, Instrument Method or Program Wizard, and the Sequence. The Dionex AS-AP autosampler verifies that the injection volume corresponds to the sample loop volume and the sample injection mode; the necessary setup commands are briefly summarized in this section.

1. A precision-cut sample loop must be used. Install the sample loop into ports 1 and 4 of the injection port according to the instructions in the *Fittings and Tubing* section.

2. Dionex AS-AP autosampler specifics: Please review the *Configuration for Large Loop and Concentrate Mode Injections* section.

   a. Instrument configuration: On the Options page for the Dionex AS-AP autosampler, enter the volume intended to load into the Loop Size field.

   b. Instrument Method Wizard or Program Wizard: On the Sampler Options page, select *PushSequentialFul*l or *PushFull* in the *Inject Mode* field, Both for *Injection Wash Mode* field.

3. Sequence

   a. Enter the injection volume in the sequence. For PushSequentialFull and PushFull modes, the injection volume must match the injection loop volume entered in the instrument configuration. If the two values are different, the sequence will not start.

Large volume injections using a monolith concentrator column

This section will review the installation of the monolith concentrator column, and briefly summarize the important commands in the Server Configuration, Program Wizard, and the Sequence. The Dionex IonSwift Monolith Anion Concentrator (MAC) column (Figure 5) are designed with very low void volume and low backpressure, to work with high purity capillary IC applications. Additionally, the Dionex IonSwift MAC concentrator columns have low sulfate chemistry to minimize baseline sulfate contamination. The monolith concentrator column must be installed without any voids between the tubing and port.

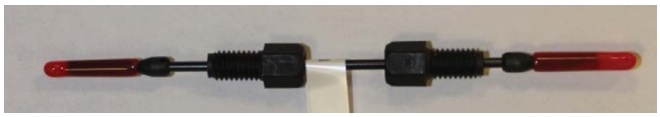

Figure 5. Dionex IonSwift concentrator column

Install the monolith concentrator column (Dionex IonSwift MAC-100 column for anions) into ports 1 and 4 of the injection port according to the instructions in the Fittings and Tubing section and the product manuals (Figure 6).[14,15]

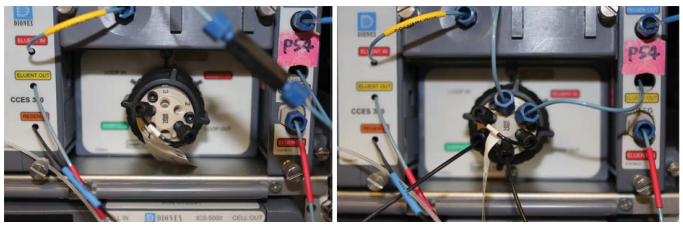

Figure 6. Dionex IonSwift Concentrator Column installed in port 1 and port 4 in the IC Cube 6-Port Valve.

Large loop injections can also be performed in pull mode, where the sample is pulled through the transfer line into the loop from the injection port normally used for waste. To use this method, reconfigure the tubing according to the AS-AP autosampler product manual and rename all commands described in the previous section from push to pull mode.[10]

1. Condition the concentrator column according to the instructions shipped with the column.

2. Dionex AS-AP autosampler specifics: Please review the *Configuration for Large Loop and Concentrate Mode Injections* section.

   a. Instrument configuration: On the Options page for the autosampler, enter the volume intended to concentrate into the Loop Size field.

b. Instrument Method Wizard or Program Wizard: On the Sampler Options page: Select *PushSequentialConcentrate* or *PushConcentrate* in the *Inject Mode* field, both for *Injection Wash Mode* field.

c. Sequence: Enter the sample volume to be concentrated. For *PushSequentialConcentrate* and *PushConcentrate* modes, the injection volume must match the injection loop volume entered in the *Server Configuration* program. If the two values are different, the sequence will not start.

Results and discussion

The most common methods to determine trace ions use either direct injection of a large sample volume or loading on a concentrator column. These techniques were applied to trace ion determinations on a capillary IC system. Data were generated by multiple chemists using separate systems and Dionex AS-AP autosamplers.

Direct injection, large loop

Direct injections are typically used to determine low µg/L (ppb) to sub-µg/L concentrations of ions.

Calibrating using direct large sample injections

Calibrating for large loop injections is done in the standard way, using standards of different concentrations to calibrate different levels. Typically a calibration curve of peak area response versus concentration is established using single or multiple injections of 3 to 5 standards covering a concentration range from slightly above the limit of quantification to slightly above the expected highest unknown sample concentration.

Chromatography results

In these capillary IC examples, Figures 7–10 show separations of 10 µL directly injected on the capillary system. While 10 µL is not usually considered a large volume, in capillary scale IC the volume is equivalent to a 1,000 µL on a 4 mm system and 250 µL on a 2 mm system. In Figure 7, trace anions in a water blank were separated on a capillary Dionex IonPac AS19 column using an electrolytically-generated KOH gradient. Concentrations as low as 2–5 ng/L chloride, sulfate, and phosphate detected. A direct injection of a ~1 µg/L mixed anion standard shows a similar separation (Figure 8). Although a Dionex CRD 200 cartridge was used, carbonate was the largest peak in both chromatograms.

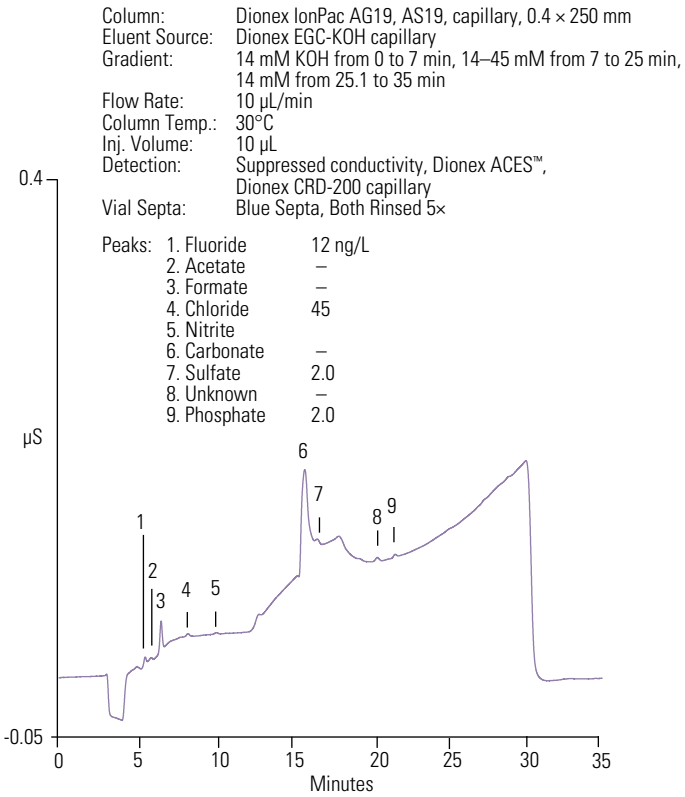

Figure 7. Trace anions in water blank sample by a 10 µL large loop direct injection.

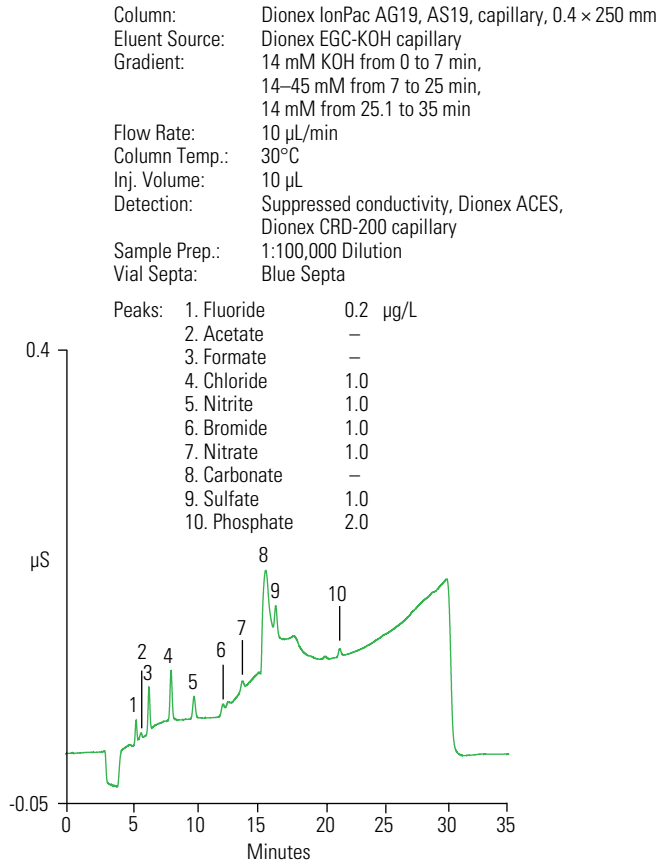

Figure 8. A large loop direct injection of a diluted Dionex Seven Anion II Standard.

Large volume injection by concentration

For larger injection volumes, it is more practical and efficient to concentrate the ions onto an ion exchange concentrator column prior to injection. Ion exchange monoliths columns with low void volumes, such as the Dionex IonSwift MAC-100 anion concentrator column, is optimized for use as concentrator columns in capillary IC. As the sample is loaded onto the concentrator column, the ions are retained and the water matrix passes to waste. The valve is switched, and the eluent elutes the ions to the guard and separator columns. The elimination of the water matrix typically increases peak response by a factor of 3–5.

Calibrating using concentrate mode

To calibrate using a concentrator column, concentrate different volumes of the same working standard from the same vial, such as 50, 100, 200 µL of ~0.5 µg/L mixed standard. Using this method, the calibration validates both the linearity of the peak responses and the efficiency of the concentrator column. However, this method will have systematic bias if there is any error in the concentration of the working standard, so special care should be taken to ensure that its concentration is accurate. The anion results using replicate injections of the three volumes were linear with regression coefficients (r^2) from 0.9993 to 0.9999.

Chromatography results

In these capillary IC examples, Figures 9 and 10 show separations of 200 µL and 100 µL, respectively, concentrated onto a Dionex IonSwift MAC-100 anion concentrator column and then eluted onto a capillary Dionex IonPac AS15 column set. The trace anions were separated by electrolytically generated 38 mM KOH. A 200 µL volume concentrated for the capillary system is equivalent to 20 mL and 5 mL for a 4 mm and 2 mm column set, respectively. In Figure 9, trace anions in a water blank sample were separated on a capillary Dionex IonPac AS15 column optimized for trace anion analysis. Carbonate and acetate are the largest peaks; chloride, sulfate, and nitrate concentration were ~25 ng/L. This water blank sample was injected from a 10 mL vial with a Teflon single injection disk (septa). An example of the ~0.1 µg/L mixed anion standard with half the volume concentrated is shown in Figure 10.

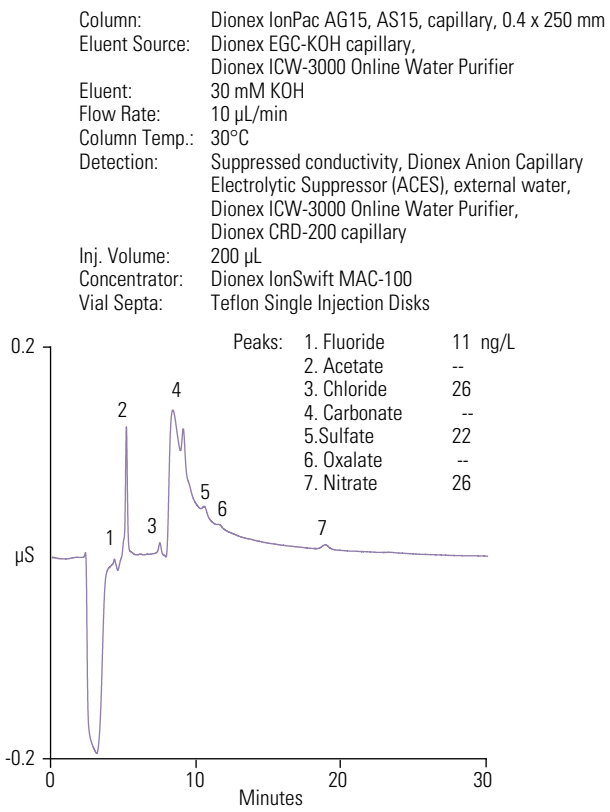

Figure 9. Trace anions in water blank injection by concentrating 200 µL on Dionex IonSwift MAC-100 concentrator column.

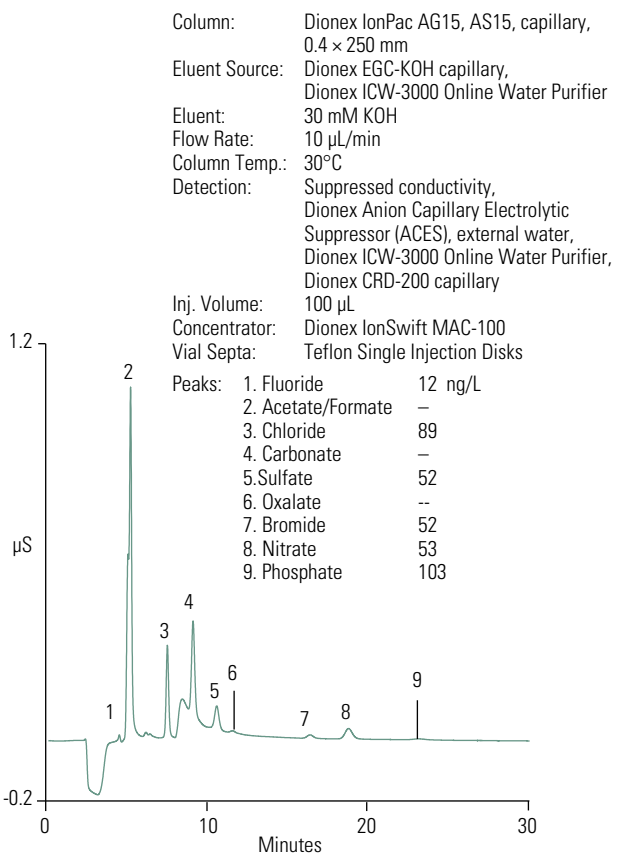

Figure 10. Trace anions standard by concentrating 100 µL on the Dionex IonSwift MAC-100 concentrator column.

Precautions

Trace ion and ultra trace analyses (low µg/L to ng/L) in ultrapure water are a challenging analytical technique that requires considerable effort, time, and patience. Many analysts experienced in trace ion analysis may initially spend several weeks to first reduce the baseline contamination to an acceptable level, then diligence to stabilize the baseline contamination, and finally to start analyzing samples. To the inexperienced analyst, trace analysis can be more challenging.

Conclusion

Trace anion determinations in UPW are demonstrated by direct injection using the Dionex AS-AP autosampler on a capillary Dionex ICS-5000 IC system. Additionally, this document thoroughly discussed techniques critical to obtain good chromatography for capillary IC and techniques critical for trace ion determinations are discussed in detail. The Dionex AS-AP autosampler, designed for cleaner and faster introduction of samples, was discussed. In conclusion, capillary IC provides results comparable to those of standard and microbore systems, and provides advantages of continuous operation, lower flow rates and lower waste generation.

References

1. Thermo Scientific Technical Note 48, Determination of Trace Anions in High-Purity Water by High-Volume Direct Injection with the EG40, Dionex LPN 1127, Sunnyvale, CA, 2001. http://tools.thermofisher.com/content/sfs/brochures/4411-TN48_LPN1127-01.pdf
2. Thermo Scientific Application Note 113, Determination of Trace Anions in High Purity Waters by High Volume/Direct Injection Ion Chromatography, Dionex LPN 0796. Sunnyvale, CA, 1996. https://tools.thermofisher.com/content/sfs/brochures/AN-113-IC-Trace-Anions-High-Purity-Waters-AN71545-EN.pdf
3. Thermo Scientific Application Update 142, Improved Determination of Trace Anions in High Purity Waters by High-Volume Direct Injection with the EG40, Dionex LPN 1291. Sunnyvale, CA, 2001. http://tools.thermofisher.com/content/sfs/brochures/4192-AU142_LPN1291-01.pdf
4. Thermo Scientific Application Note 146, Determination of Trace Anions in High-Purity Waters by Ion Chromatography with IonPac AS17 Using High Volume Direct Injection with the EG40, Dionex LPN 1507. Sunnyvale, CA, 2003. https://tools.thermofisher.com/content/sfs/brochures/AN-146-IC-Trace-Anions-High-Purity-Waters-IonPac-AS17-EG40-AN71550-EN.pdf
5. Thermo Scientific Application Update 157, Using a Reagent-Free Ion Chromatography System to Monitor Trace Anion Contamination in the Extracts of Electronic Components, Dionex LPN 1853. Sunnyvale, CA, 2006. https://tools.thermofisher.com/content/sfs/brochures/AU-157-Monitor-Trace-Anion-Contamination-Extracts-Electric-Components-LPN1853.pdf
6. Thermo Scientific Application Note 222, Determination of Parts-Per-Trillion Concentrations of Strontium by Pre-Concentration with Ion Chromatography and Suppressed Conductivity Detection, Dionex LPN 2182. Sunnyvale, CA, 2009. http://tools.thermofisher.com/content/sfs/brochures/71299-AN222-IC-StrontiumDetecton-08Apr09-LPN2182.pdf
7. Thermo Fisher Scientific. Application Update 169, Determination of Silicate and Inorganic Anions in High Purity Water Using Sequential Detection and AutoPrep, Dionex LPN 2188. Sunnyvale, CA, 2009. https://tools.thermofisher.com/content/sfs/brochures/70947-AU169-Silicate-SeqDet-AutoPrep-18Mar09-LPN2188.pdf
8. Thermo Scientific Instructions: Connecting the ICW-3000 to a Capillary Ion Chromatography System, Dionex LPN 065459 rev 01.
9. Thermo Scientific Technical Note 115: Using an On-line Water Purifier for Trace Ion Determinations in Ultra Pure Water (UPW), Dionex LPN 3081. Sunnyvale, CA 2012.
10. Thermo Scientific Dionex ICS Series AS-AP Autosampler Operator's Manual, Dionex Doc. No 065361. Sunnyvale, CA, 2011.
11. Thermo Scientific Dionex ICS-5000 Ion Chromatography System Installation Instructions, Dionex Doc. No 065343. Sunnyvale, CA, 2011.
12. Thermo Scientific Dionex ICS-5000 Ion Chromatography Operator's Manual, Dionex Doc. No 065342. Sunnyvale, CA, 2011.
13. Thermo Scientific Technical Note 113, Practical Guidance for Using Capillary Ion Chromatography, Dionex LPN 3043. Sunnyvale, CA, 2011. https://tools.thermofisher.com/content/sfs/brochures/TN113-IC-Capillary-Anion-Guidance-28Feb2012-LPN3043.pdf
14. Thermo Scientific Product Manual for IonSwift Monolith Anion Concentrator (MAC), Dionex Doc. No 065387. Sunnyvale, CA, 2010.

Find out more at **thermofisher.com/IC**

ThermoFisher SCIENTIFIC