Fast Determinations of Inorganic Ions in Salton Sea Samples Using a High-Pressure IC System

Terri Christison and Linda Lopez
Thermo Fisher Scientific, Sunnyvale, CA, USA

Technical Note 130

Key Words
ICS-5000+, IonPac AS18-4 µm, IonPac CS12A, Anions, Cations, Environmental, HPIC, Saline Solutions

Goal
Demonstrate fast separations of inorganic ions in a saline solution samples using a high pressure Thermo Scientific™ Dionex™ ICS-5000+ HPIC IC system

Introduction
Monitoring salinity levels in estuarine ecosystems is critical to preventing salinity-specific diseases. In the Chesapeake and Delaware bays, for example, pathogens infecting oysters are restricted to areas that fall within discrete salinity levels. The Salton Sea, presently a lake with a higher salt content (20 to 44 g/L) than the ocean, was formed in 1905–1907 when the Colorado River breached irrigation canals and flooded the area for more than a year.[1] Because the middle of the sea is at lower elevation than the outlet, water is lost primarily through evaporation, leaving dissolved salts behind and gradually raising salinity. The Department of Fish and Game introduced saline tolerant fish. Although, as the salinity levels rise, the lake's waters become increasingly inhospitable to fish and most other creatures. Brine shrimp and alkali flies are the exception, however. Many species of migratory and nesting birds feed on the shrimp and fly blooms. As a result, any ignorance will make the lake uninhabitable. This in turn will impact migrating wildlife, migration patters and recreational activities.

Ion chromatography uses ion exchange resins to separate ions in solutions, making it ideally suited to the analysis of high salinity water samples. With recent advances in High Pressure Ion Chromatography (HPIC™), the continuous operation ability at 5000 psi in both analytical and capillary scale formats, permit fast, high-throughput analysis without sacrificing resolution. When combined with the power of Reagent-Free™ Ion Chromatography (RFIC™) systems, it provides precise eluent generation with improved resolution of closely eluting peaks. As a result, far more accurate quantification and reliable results are possible.

In this study we demonstrate the fast separations of inorganic anions and cations in a Salton Sea surface water sample and a neighboring municipal drinking water sample using ion-exchange chromatography on a high pressure capable Thermo Scientific Dionex ICS-5000+ HPIC system. The analysis times for inorganic anions and cations on separate ion-exchange columns optimized for fast separations were reduced from approximately 10 to 4 min by increasing the flow rate 2.5-fold.

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Equipment

- High Pressure Dionex ICS-5000+ HPIC RFIC system
  - ICS-5000+ SP/DP Pump module
  - ICS-5000+ EG Eluent Generator module with high pressure degas module
  - ICS-5000+ DC Detector/Chromatography module
  - Thermo Scientific Dionex AS-AP Autosampler
  - Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data system (CDS) 6.8 or 7.1

Reagents and Standards

- 18 MΩ-cm degassed deionized water
- Thermo Scientific Dionex Combined Six Cation Standard II (Dionex P/N 046070)
- Thermo Scientific Dionex Combined Seven Anion Standard II (Dionex P/N 057590)
- Fisher Scientific reagents, ACS grade

Samples

A surface sample was collected from the Salton Sea at Bombay Beach, CA. A municipal drinking water sample was also collected in a neighboring desert city for comparison.

Conditions

Anions	
Column:	Thermo Scientific™ Dionex™ IonPac™ AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
Eluent Source:	Thermo Scientific Dionex EGC 500 KOH Eluent Generator Cartridge Thermo Scientific Dionex CR-ATC 500 Continuously Regenerated Anion Trap Column
Eluent:	23 mM KOH
Flow Rate:	0.25, 0.35, 0.45, 0.55 mL/min for flow rate experiments 0.55 mL/min for samples
Inj. Volume:	5 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor™, recycle; 15, 26, 32 mA
Background Conductance:	1–2 µS
Noise:	2–3 nS
System Backpressure:	2000*–4300 psi

Cations	
Columns:	Dionex IonPac CG12A-5µm, 3 × 30 mm Dionex IonPac CS12A-5µm, 3 × 150 mm
Eluent Source:	Dionex EGC 500 MSA cartridge, CR-CTC 500 trap column
Eluent:	35 mM MSA
Flow Rate:	0.25, 0.50, 0.75 mL/min for flow rate experiments 0.75 mL/min for samples
Inj. Volume:	25 µL
Column Temp:	30 °C
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CSRS™ 300 Cation Self-Regenerating Suppressor, recycle, A: 26, B: 52, C: 77 mA
Background Conductance:	0.4–0.6 µS
Noise:	2–3 nS
System Backpressure:	2000*–3100 psi

** Backpressure tubing was added prior to the injection valve for those conditions running below <2000 psi to bring the total system pressure above 2000 psi needed for the Dionex EGC 500 cartridge.*

Standard and Sample Preparation

Prepare the IC standards from individual or combined standards such as Dionex Combined Six Cation II Standard and Seven Combined II Standard. The concentrations of each analyte in the flow rates experiments are listed in Figure 2. The Salton Sea surface sample was diluted 1000-fold with deionized water to minimize overloading the columns and filtered with a 0.20 µm, IC syringe filter to remove particulates, visible organisms, and microorganisms prior to analysis. The municipal drinking water sample was analyzed without any sample preparation.

Tip: It is important to use 18 MΩ-cm resistivity, deionized water for standards, eluent, and autosampler flush solution. It is recommended to degas the deionized water intended for eluent used for anion determinations. (An appropriate degassing method is vacuum filtration.) Using deionized water with resistivity less than 18 MΩ-cm can reduce sensitivity, introduce contamination, and affect calibration, thereby resulting in inaccurate quantification. Results can vary and contamination introduced from samples can affect the chromatography.

Instrument Setup

Tip: To achieve the best chromatography with high pressure IC, it is important to use high pressure connectors and ferrules (see Table 1) for all connections prior to the suppressor. The high pressure Dionex ICS-5000⁺ HPIC Reagent-Free IC system is designed to operate from 2000 to 5000 psi. To set up this application, plumb the consumables and modules of the Dionex ICS-5000⁺ HPIC system, according to Figure 1.

Install and hydrate the Dionex EGC 500 cartridges, Dionex CR-TC 500 trap columns, and 2 mm Dionex SRS 500 suppressors according to the product manual instructions. Complete the installation according to flow diagram. Use high pressure connectors and ferrules (blue) for all of the fittings from the pump to prior the suppressor. Standard pressure fittings can be used for the suppressor and detector connections. Detailed instructions are described in Technical Note (TN) 129, the product manuals, and the instrument installation and operator's manuals.[2–5]

Table 1. Consumables list.

Product Name	Type	Dionex Part Number
Dionex EGC 500 KOH	Anion Eluent Generator cartridge*	075778
Dionex CR-ATC 500	Anion electrolytic trap column*	075550
Dionex IonPac AG18-4µm	Anion guard column	076037
Dionex IonPac AS18-4µm	Anion separation column	076036
Dionex ASRS 300	Anion suppressor*	064555
Dionex EGC 500 MSA	Cation Eluent Generator cartridge*	075779
Dionex CR-CTC 500	Cation electrolytic trap column*	075551
Dionex IonPac CG12A-5µm	Cation guard column, 3 × 30 mm	057184
Dionex IonPac CS12A-5µm	Cation separation column, 3 × 150 mm	057185
Dionex CSRS 300	Cation suppressor*	064557
Dionex HP Degas Module	High pressure analytical Degas module*	075522
Dionex HP Fittings (blue)	Bolts/Ferrules*	074449/ 074373

** High pressure device*

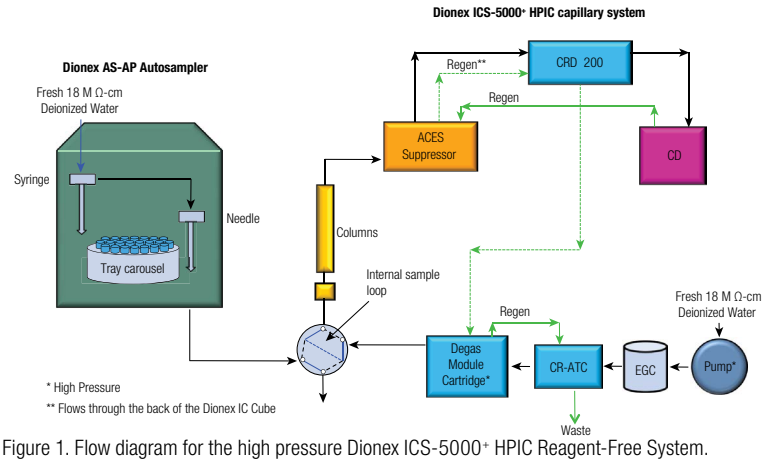

Figure 1. Flow diagram for the high pressure Dionex ICS-5000⁺ HPIC Reagent-Free System.

Results and Discussion

In this application inorganic cations in a diluted seawater sample and an undiluted municipal drinking water sample were separated on a microbore-size (i.d. 3 mm) Dionex IonPac CS12A-5 µm cation-exchange column using 35 mM MSA. Similarly, inorganic anions in the same samples are determined on a smaller particle version of the 2 mm i.d. Dionex IonPac AS18-4µm anion-exchange column using 23 mM KOH. These 150 mm length columns were optimized for rapid separations of inorganic ions. Additionally, the smaller particle size, 4 µm anion-exchange column permits more efficient separations than the 7.5 to 11 µm particle-size columns with no significant loss in resolution. Eluents were electrolytically generated using Dionex EGC 500 eluent generator cartridges designed to deliver precise and accurate eluent inline with continuous operating pressures up to 5000 psi. Using inline eluent generation precludes manual eluent preparation, thereby eliminating inaccuracies as result of eluent preparation errors and operator-to-operator variability. Analytes are detected using suppressed conductivity which increases the signal-to-noise by suppressing the background conductivity while increasing the signal of the analytes.

Flow Rate Experiments

To demonstrate the fastest separations while retaining nearly baseline resolution, the flow rates were increased incrementally from 0.25 to 0.55 mL/min for anions and 0.25 to 0.75 mL/min for cations. Figure 2 shows the separation of an eight anion standard at three different flow rates, 0.25, 0.30, and 0.38 mL/min. These data demonstrate near-baseline resolution of all peaks, with less than 6 min fast analysis times for the fastest flow rate. Figure 3 shows the separations of a six cation standard. Flow rates on the cation column were increased 3× the standard flow rate, resulting in 4 min run times with system backpressures of 3100 psi. Using this fast separation, samples typically requiring 9 min per sample run can now be analyzed in 4 min, thereby increasing the daily throughput from 50 to 112 samples per day.

Column:	Dionex IonPac AG18-4µm, 2 × 30 mm Dionex IonPac AS18-4µm, 2 × 150 mm
Eluent Source:	Dionex EGC 500 KOH cartridge
Eluent:	23 mM KOH
Flow Rate:	A: 0.25, B: 0.30, C: 0.38 mL/min
Inj. Volume:	5 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS 300, recycle A: 15, B: 18, C: 22 mA

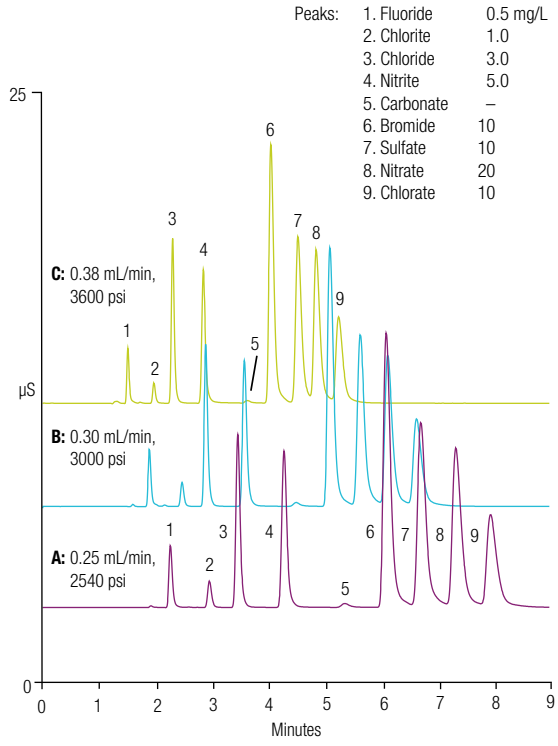

Figure 2. Fast separations of an anion standard using high pressure IC.

Column:	Dionex IonPac CG12A-5µm, 3 × 30 mm Dionex IonPac CS12A-5µm, 3 × 150 mm
Eluent Source:	Thermo Scientific Dionex EGC 500 MSA cartridge
Eluent:	35 mM Methanesulfonic acid
Flow Rates:	A: 0.25, B: 0.50, C: 0.75 mL/min
Inj. Volume:	25 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity Dionex CSRS 300, 2 mm, recycle, A: 26, B: 52, C: 77 mA
IC System:	Dionex ICS-5000⁺ HPIC system
Sample Prep.:	500-fold dilution

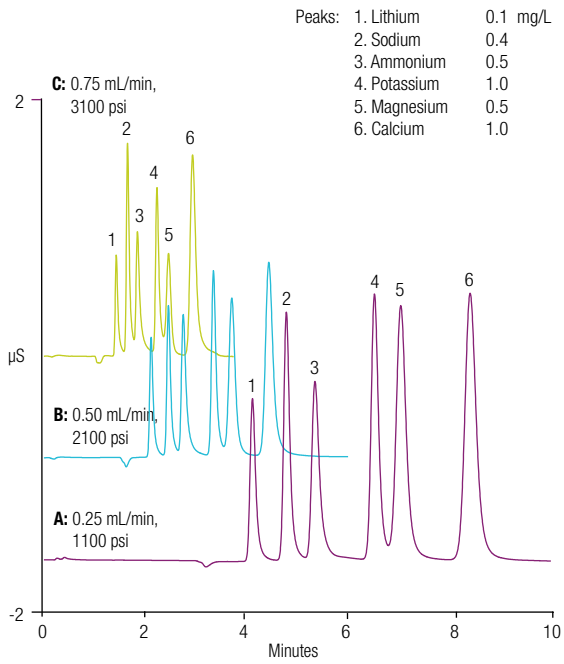

Figure 3. Fast separations of Dionex Combined Six Cation II Standard using high pressure IC.

Sample Analysis

In Figures 4 and 5, the ionic content of a 1000-fold diluted Salton Sea sample is compared to a municipal drinking water sample from a nearby city. The Salton Sea sample contains mostly sodium, sulfate, and chloride (20 to 30 g/L) with lesser amounts of magnesium and calcium (~2 g/L). The municipal drinking water sample contains proportionally higher concentrations of sodium, sulfate, and calcium (20, 30, and 40 mg/L, respectively) than the Salton Sea sample. The chromatograms demonstrate the differences in water sources of the Salton Sea and local water source.

Column:	Dionex IonPac AS18-4µm, 4 × 150 mm Dionex IonPac AG18-4µm, 4 × 150 mm
Eluent Source:	Dionex EGC-KOH with Dionex CR-ATC
Eluent:	23 mM KOH
Flow Rate:	0.38 mL/min
Inj. Volume:	5 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS 300, recycle, 22 mA
Samples:	A: Municipal drinking water B: Salton Sea surface water sample
Sample Prep.:	A: Diluted 5-fold, B: Diluted 1000-fold, filtered 0.45 µm

Peaks:		A	B
	1. Fluoride	0.1 mg/L	–
	2. Chloride	11.8	31.1 mg/L
	3. Carbonate	–	–
	4. Sulfate	29.9	18.3
	5. Nitrate	9.0	–

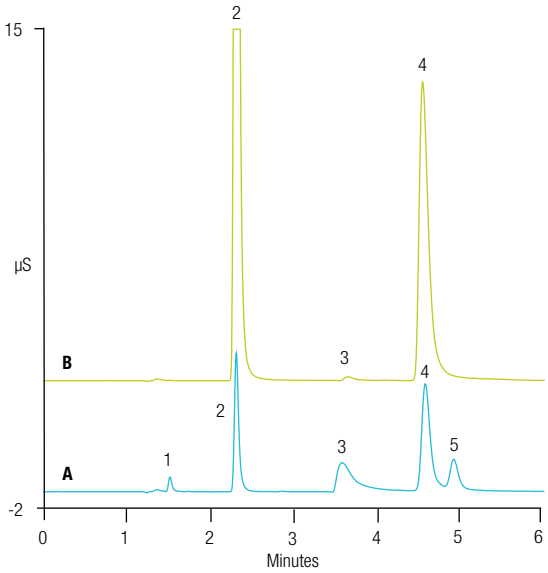

Figure 4. Fast anion determinations of the Salton Sea area water samples using high pressure IC.

Column:	Dionex IonPac CG12A-5µm, 3 × 30 mm Dionex IonPac CS12A-5µm, 3 × 150 mm
Eluent Source:	Dionex EGC 500 MSA cartridge
Eluent:	35 mM Methanesulfonic acid
Flow Rates:	0.75 mL/min
Inj. Volume:	25 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity Dionex CSRS 300, 2 mm, recycle 77 mA
IC System:	Dionex ICS-5000⁺ HPIC system
Sample Prep.:	A: Undiluted B: 1000-fold dilution, filtered, 0.20 µm
Samples:	A: Municipal drinking water B: Salton Sea Surface sample

Peaks:		A	B
	1. Sodium	23.2 mg/L	20.0 g/L
	2. Potassium	3.60	0.40
	3. Magnesium	9.51	2.05
	4. Calcium	42.5	1.74

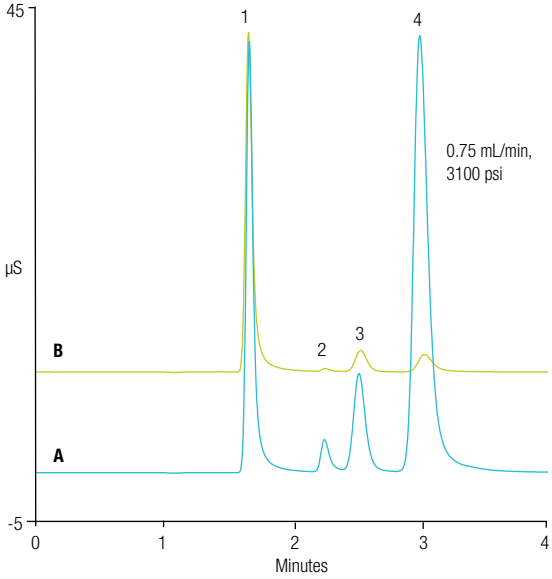

Figure 5. Fast cation determinations of the Salton Sea Area water samples using high pressure IC.

Conclusion

This application demonstrates the advantages of high pressure IC using a Dionex ICS-5000+ HPIC system to provide fast high resolution separations on microbore columns. The high back pressure capability of the Dionex ICS-5000+ HPIC system permits fast separations across standard bore, microbore, and capillary scale formats.

Additional information on inorganic anion and cation determinations in environmental water and saline water samples using 7 to 11 µm particle standard bore and microbore IC columns are reviewed in application notes AN141, AN154, and AN260.[6–8] High pressure separations using capillary IC are discussed in application brief AB141 and Environmental Capillary IC Applications at the Dionex Capillary IC Library website.[9,10]

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