

# Fundamentals of Capillary Ion Chromatography

*Peter Bodsky and Frank Hoefler, Thermo Fisher Scientific, Sunnyvale, CA USA*



## Overview

•**Purpose:** In this work, we highlight the fundamental differences between conventional IC (4 mm and 2 mm) and Capillary Ion Chromatography.

•**Methods:** Like conventional IC, Capillary Ion Chromatography systems utilize ion exchange and eluent generation devices to generate high-purity acid and base solutions as eluents for use in ion chromatography systems. When using these devices, the operator simply adds water to the system and these devices generate the desired chemistry.

•**Results:** The combined use of Reagent-Free™ Ion Chromatography (RFIC™) and Capillary IC provides new opportunities to perform IC with less maintenance and improved ease of use.

## Introduction

Ion chromatography (IC) is a widely used analytical technique for determination of anionic and cationic analytes in various sample matrices. In modern IC systems, high purity acid, base, or salt eluents are generated electrolytically using deionized water as the carrier. The Reagent-Free Ion Chromatography (RFIC) systems with electrolytic eluent generation make it possible to perform a wide range of ion chromatographic separations using only deionized water as the carrier. For many applications, the RFIC systems provide improved performance with increased sensitivity and the flexibility to perform isocratic and gradient separations. In addition to saving time, labor, and operating costs, the RFIC systems eliminate errors and problems associated with manual eluent preparation and offer users the benefits of simplicity, ease of use, and improved method reproducibility.

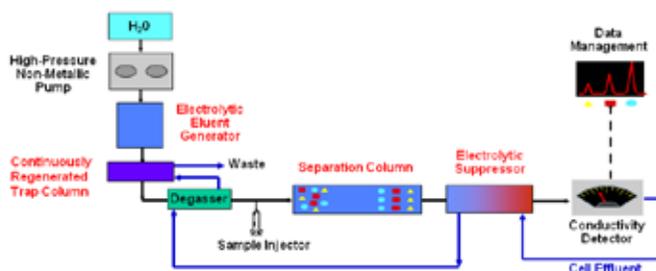
Coupling RFIC technology with Capillary scale systems provides a very unique feature set that offers the end user greater flexibility and ease of use with respect to system operation and readiness.

## Experimental

All experiments were performed using Thermo Scientific Dionex ICS-5000 capillary RFIC systems with electrolytic eluent generation. A typical Dionex ICS-5000 system consists of a dual pump module (DP), an eluent generator (EG) module, and a detector/ chromatography module (DC). The modular design of the Dionex ICS-5000 systems allows users to quickly configure and customize components for a wide range of applications. The system can be configured as a dual-channel capillary RFIC system, a dual-channel conventional RFIC system, or a dual-channel RFIC system supporting both conventional and capillary-scale IC separations. The Dionex ICS-5000 RFIC systems are fully supported by Thermo Scientific Dionex Chromeleon™ 6.8 and 7 software. Several conventional-scale and capillary-scale Thermo Scientific Dionex IonPac™ anion-exchange and cation-exchange columns were used. Current capillary-scale systems support high-pressure eluent generation as well as manually prepared eluents.

The block diagram of key components used in a typical RFIC system is shown in Figure 1. A high-pressure pump is used to deliver a stream of deionized water into an eluent generator cartridge (Thermo Scientific Dionex EGC) where the high-purity base or acid eluent is generated electrolytically. A continuously regenerated trap column (Thermo Scientific Dionex CR-TC) is used to remove trace contaminants in the eluent. A high-pressure degasser containing a gas permeable tubing is used to remove hydrogen or oxygen gas formed electrolytically. There are several other downstream system components including a sample injector, a separation column, and an electrolytic suppressor. In the system shown, the conductivity detector effluent is routed through the regenerant chambers of the electrolytic suppressor, the Dionex CR-TC, and the high-pressure degasser assembly before going to waste. Therefore, the RFIC system makes it possible to perform the entire IC separation process using only deionized water as the carrier.

FIGURE 1. Block diagram of key components in an Capillary RFIC system.



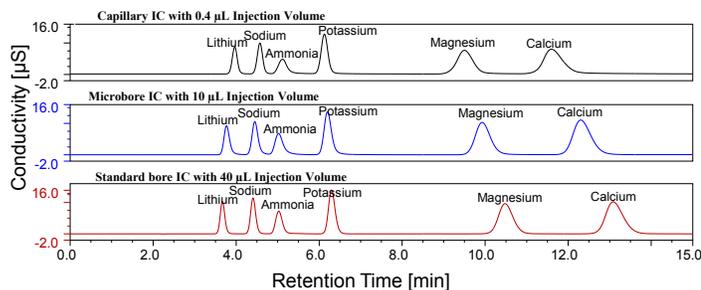
The Dionex ICS-5000 RFIC systems use electrolytic eluent generator cartridges (Dionex EGC) to generate potassium hydroxide (KOH) or methanesulfonic acid (MSA) eluents on-line using deionized water as the carrier stream. To generate a KOH solution, deionized water is pumped through the eluent generation chamber and a DC current is applied between the device's anode and cathode. Under the applied electrical field, water is oxidized to form H<sup>+</sup> ions and oxygen at the anode. Water is also reduced to form OH<sup>-</sup> ions at the cathode. K<sup>+</sup> ions migrate from the electrolyte reservoir through the ion-exchange connector into the KOH generation chamber and combine with OH<sup>-</sup> ions generated at the cathode to form a KOH solution. The concentration of KOH formed is directly proportional to the applied current and inversely proportional to the flow rate.

When comparing 4 mm systems to capillary scale systems, it is instructive to remember that there is a scale-down of the geometry by a factor of 10. Figure 2 illustrates the primary differences.

FIGURE 2. Capillary IC – The dimension of scale.

	Analytical	Capillary
Column i.d.	4 mm	0.4 mm
Flow Rate	1.0 mL/min	10 µL/min
Injection Volume	25 µL	0.4 µL
Eluent Consumption / Waste Generated	43.2 L/month	0.432 L/month
EGC Lifetime (@75 mM)	28 Days	18 months
Mass Detection Limits	7000 fg	70 fg

**FIGURE 3. Overlay of chromatograms from 4 mm, 2 mm and 0.4 mm – all with optimum injection volume.**



**FIGURE 4. Overlay of chromatograms from 4 mm, 2 mm and 0.4 mm – all with the same 0.4 µL injection volume.**

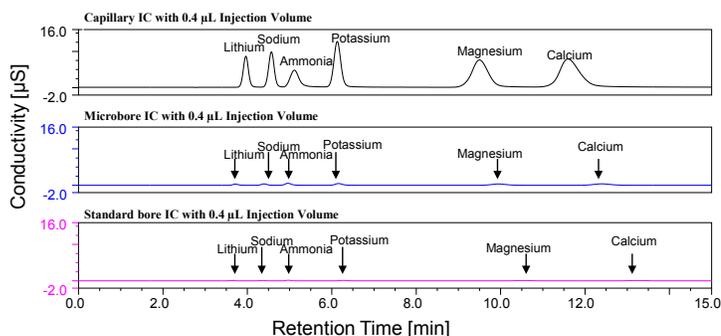
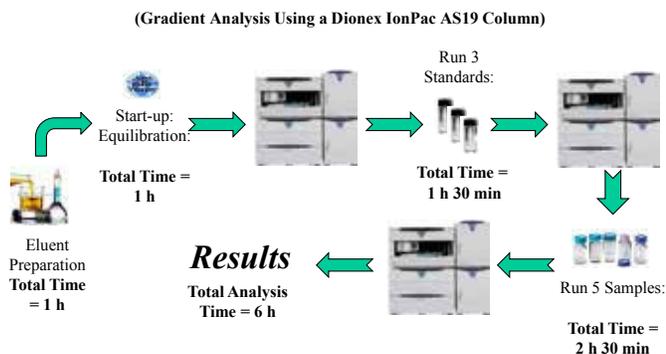


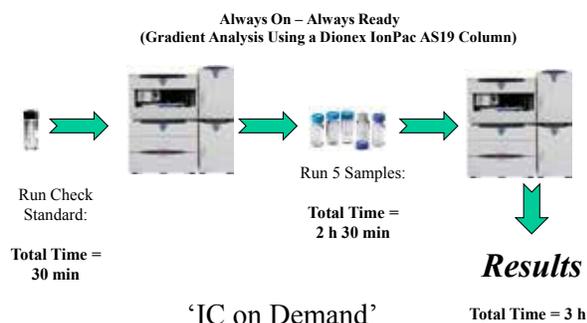
Figure 3 illustrates a comparison between a 4 mm, 2 mm, and a 0.4 mm system and each injected with their optimal sample volumes. In Figure 4, the injection volume (0.4 µL) is uniform across each column geometry. This comparison illustrates the inherent improvement in mass sensitivity when we go from a standard bore (4 mm) column to a capillary scale column.

**FIGURE 5. Typical workflow: traditional IC.**



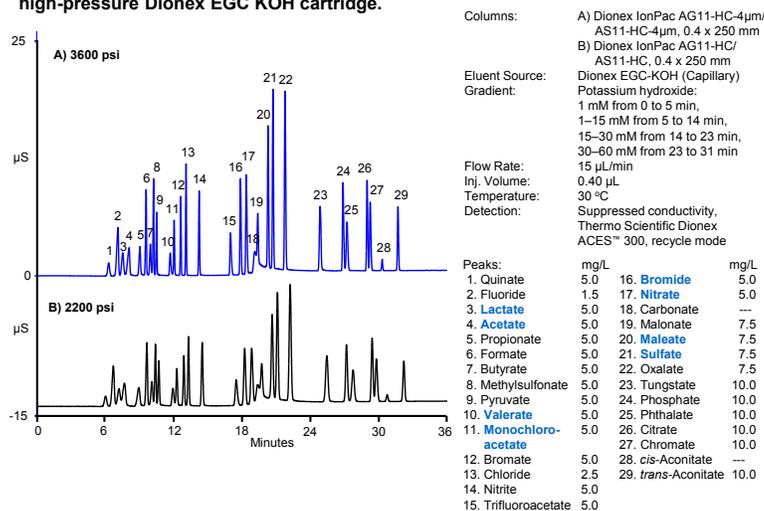
When we look at a typical IC system, we are able to describe a “traditional” workflow (Figure 5). In this workflow are the common steps associated with daily (routine) IC operation: making mobile phase, system equilibration, and system calibration. If one compares the typical workflow of a standard IC system to that of a Capillary IC system (Figure 6), we see that the Capillary IC system offers a simplified overview. The Capillary IC system does not require any mobile phase preparation. Since the system is always left in operation, the frequency of calibration is considerably less. The use of a check standard to verify that the system is still in calibration is sufficient.

FIGURE 6. Typical workflow: capillary IC operated continuously.



The overall time savings when comparing a capillary scale system to 4 mm system is roughly 3 hours per day. These savings are largely derived from the elimination of the mobile phase preparation, system equilibration, and calibration steps.

FIGURE 7. Comparison of gradient separations of 29 anions using capillary Dionex IonPac AS11-HC-4 $\mu$ m and Dionex IonPac AS11-HC columns and a high-pressure Dionex EGC KOH cartridge.

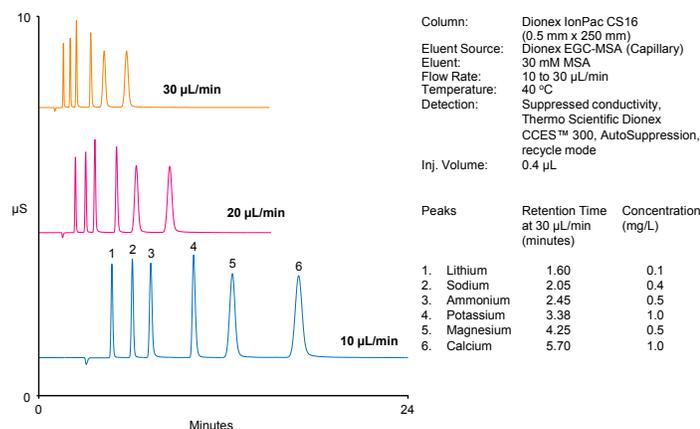


High-pressure Dionex ICS-5000 capillary HPIC systems with smaller particle-size columns are capable of providing highly reproducible separations of target analytes that are difficult to achieve using standard IC systems. Figure 7 shows a comparison of high-resolution separations of 29 inorganic and organic anions obtained using capillary Dionex IonPac AS11-HC-4 $\mu$ m and Dionex IonPac AS11-HC columns. A hydroxide gradient from 1 to 60 mM KOH was performed at 0.40  $\mu$ L/min. All peaks are sharper, and separations of closely eluting analytes such as lactate and acetate, valerate and monochloroacetate, bromide and nitrate, and maleate and succinate are improved using the more efficient 4  $\mu$ m column.

The high-pressure Dionex ICS-5000 capillary HPIC™ system provides an ideal platform to perform fast RFIC separation of common anions and cations. Figure 8 shows the fast separation of common cations using a capillary Dionex IonPac CS16 column. The separation flow rate was varied from 10 to 30  $\mu$ L/min to influence the separation process. By performing separation using 30 mM MSA at 30  $\mu$ L/min, six common cations were separated in less than 6 min while maintaining sufficient resolution of target analytes.

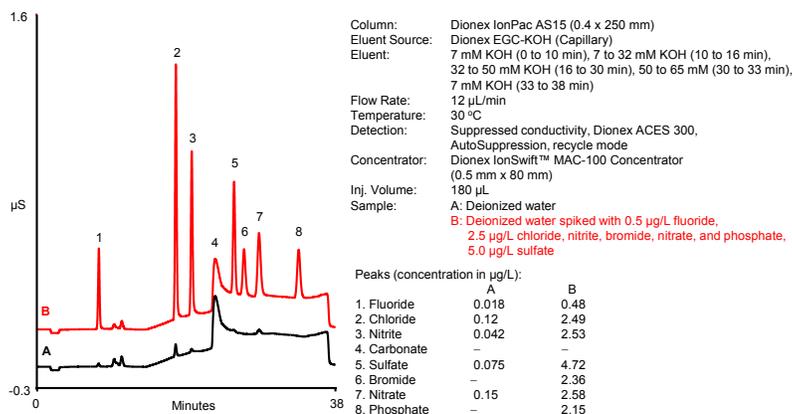
Compared to conventional-scale IC systems using 4 mm i.d. columns, the capillary IC systems using 0.4 mm i.d. columns provide increased mass sensitivity. This is due to the fact that, for the same amounts of analytes injected onto both columns, the concentrations of separated analytes going through the conductivity detector in the 0.4 mm column systems are 100 times of those in the 4 mm column system.

**FIGURE 8. Fast separation of six cations on a capillary Dionex IonPac CS16 column.**



Because of this increased mass sensitivity, the capillary IC systems offer improved performance in trace analysis of target analytes. A 10 µL injection on a capillary IC system is equivalent to a 1 mL injection on the conventional IC system. Figure 9 shows the use of a capillary RFIC system in the determination of inorganic anions at trace concentration using a capillary Dionex IonPac AS15 as the separation column. By direction injection of 180 µL of samples (equivalent to 18 mL on a conventional system), low ppt levels of target anions can be quantified.

**FIGURE 9. Separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS15 column.**



## Conclusion

- Capillary RFIC systems provide new platforms to improve the determination of target analytes in different sample matrices
- RFIC systems offer significant benefits in terms of ease of use and improved performance of IC methods
- The development of electrolytic eluent generation technology and RFIC systems has fundamentally changed the practice of ion chromatography
- The combined use of RFIC systems fitted with new high-pressure EGC cartridges and new IC columns packed with resins of smaller particle sizes (e.g., 4 µm) provides new opportunities to perform fast and high resolution IC separations.

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**China** +852 2428 3282

**Denmark** +45 70 23 62 60  
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**Sweden** +46 8 473 3380

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