New Developments in Capillary Ion Chromatography Systems Using On-Line Electrolytic Eluent Generation

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Executive Summary

Capillary IC systems offer substantial benefits over conventional IC platforms, including higher mass sensitivity, improved separation efficiency and/or speed, smaller sample volumes, reduced eluent consumption, and continuous system operation. Thermo Scientific™ Dionex™ ICS-5000 Capillary Reagent-Free™ IC (RFIC™) systems utilize on-line electrolytic eluent generation to maximize the performance and robustness of both conventional and capillary IC methods. Convenient and cost-effective, these systems are ideally suited for determination of trace levels of ionic analytes in matrix-rich and volume-limited samples across multiple applications.

Key Words

ICS-5000, Reagent-Free IC, RFIC, Capillary IC, Electrolytic eluent generation

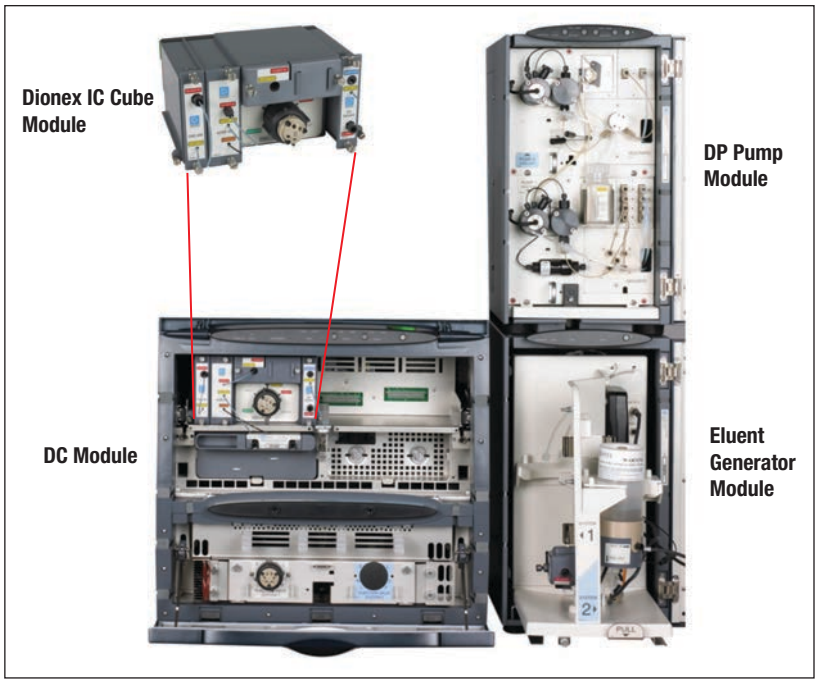

Figure 1. An ICS-5000 capillary RFIC system.

Introduction

There has been increasing interest in the development of capillary IC systems and methods for determination of ionic species. The practice of ion chromatography in capillary format offers a number of advantages. Because the eluent consumption is very low, capillary IC systems can be operated continuously and thus, are always on and always ready for analysis. Capillary IC systems offer improved compatibility with applications where amount of sample is limited. Capillary IC systems provide improved performance for determination of target analytes at trace levels. The use of capillary columns can improve separation efficiency and/or speed. The operation of capillary IC systems at low-flow rates improves the system compatibility with a mass spectrometer. In addition, the use of capillary separation columns opens the door for the possibility of offering new selectivity for difficult applications using new columns packed with stationary phases that are more costly and difficult to prepare.

This white paper describes the development of capillary RFIC systems with on-line electrolytic eluent generation. The key components of new Dionex ICS-5000 capillary RFIC systems are discussed. The analytical capabilities of Dionex ICS-5000 capillary RFIC systems for the determination of target ionic analytes using suppressed conductivity will be demonstrated. The use of Dionex ICS-5000 capillary RFIC systems for determination of carbohydrates using pulsed amperometric detection will also be presented.

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Experimental

Figure 1 shows the Dionex ICS-5000 RFIC system, the first IC system on the market capable of performing both conventional- and capillary-scale IC separations. A typical Dionex ICS-5000 system consists of a Dual-Pump module (DP), an Eluent Generator module (EG), and a Detector/Chromatography module (DC). The Dionex ICS-5000 systems support RFIC technologies including eluent generation as well as manually prepared eluents for both conventional- and capillary-scale separations. The modular design of the Dionex ICS-5000 systems allows users to quickly configure and customize components for a wide range of applications. For example, a Dionex ICS-5000 RFIC 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.

One novel feature of the Dionex ICS-5000 RFIC system is the Thermo Scientific™ Dionex™ IC Cube™ module. The Dionex IC Cube module is a small housing that resides in the DC. This module houses an EG degasser cartridge, a capillary column cartridge, an injection valve, a capillary suppressor cartridge, and an optional carbonate removal device (CRD) cartridge. The unique designs of the Dionex IC Cube module and associated cartridges simplify the plumbing of a capillary IC system by reducing the number of operator-made fluidic connections by 50%. The Dionex ICS-5000 RFIC systems are fully supported by Thermo Scientific™ Dionex™ Chromeleon™ 6.8 and 7.0 Chromatography Data System software.

The key components of a Dionex ICS-5000 capillary RFIC system with suppressed conductivity detection is illustrated in Figure 2. Table 1 summarizes the typical conventional and capillary RFIC system operating parameters. Figure 3 shows the block diagram of a Dionex ICS-5000 capillary RFIC system configured with a capillary electrochemical detector. The capillary electrochemical detector operated in the pulsed amperometric mode is fitted with a new palladium hydrogen (PdH) reference electrode.

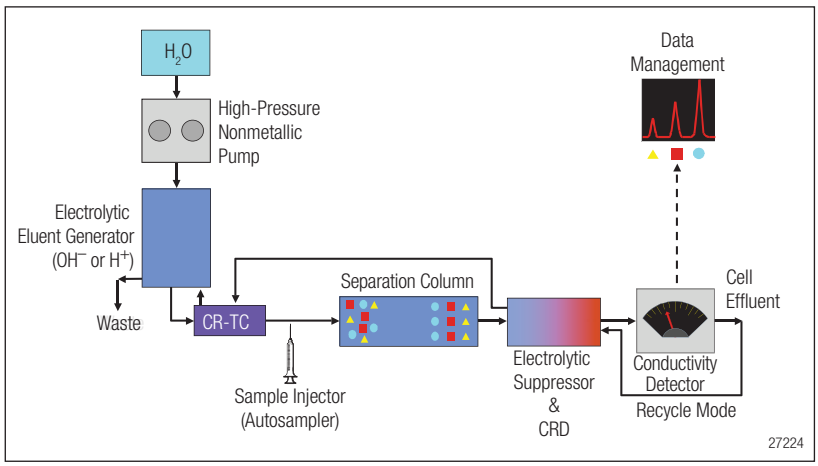


Figure 2. Block diagram of a capillary RFIC system with suppressed conductivity detection.

Table 1. Typical conventional and capillary RFIC system operating parameters.

	Conventional IC	Capillary IC
Column i.d.	4 mm	0.40 mm
Flow Rate	1.0 mL/min	10 µL/min
Injection Loop	25 µL	0.4 µL
Suppressor Dead Volume	60 µL	0.6 µL
EG Current (50 mM KOH)	80.4 mA	0.804 mA
K+ Consumption/Year	26.3 mol (50 mM KOH)	0.263 mol (50 mM KOH)
H_2O Consumption/Year	525.6 L	5.256 L

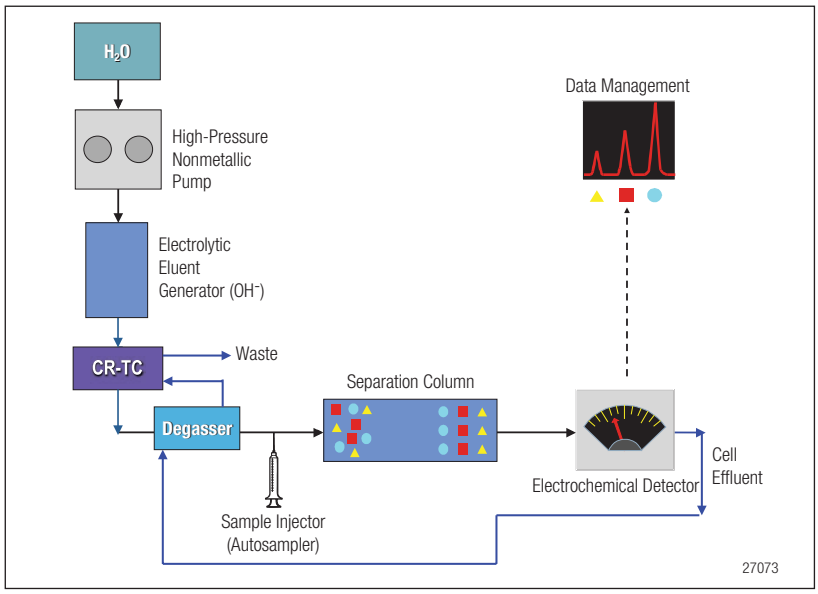


Figure 3. Block diagram of a capillary RFIC system with electrochemical detection.

Results and Discussion

The Dionex ICS-5000 capillary RFIC systems use capillary electrolytic eluent generator cartridges (EGC) to generate potassium hydroxide (KOH) or methanesulfonic acid (MSA) eluents on-line using deionized water as the carrier stream. The electrolytic eluent generator in the capillary format provides an ideal eluent generation and delivery platform for both isocratic and gradient capillary separations. The electrolytic suppressor is another key component of a capillary RFIC system. The desired characteristics of capillary IC suppressors include low dead volume, high suppression capacity, and low baseline noise. The capillary IC suppressors must be capable of continuous operation, easy to operate without the need to have external acid or base regenerant solution, and also be rugged and reliable. It is desirable that the capillary IC suppressors are compatible with mass spectrometry detection. The capillary-scale suppressors developed in this study offer these desired characteristics.

The Dionex ICS-5000 capillary RFIC systems with suppressed conductivity detector are capable of providing performance equivalent to those used in the conventional-scale RFIC systems. Figure 4 shows the isocratic separation of common anions obtained using a capillary Thermo Scientific™ Dionex™ IonPac™ AS19 column. For 30 consecutive injections performed, the retention time relative standard deviation (RSD) ranges from 0.060% (bromide) to 0.091% (fluoride), and the peak area RSD ranges from 0.24% (sulfate) to 0.50% (fluoride).

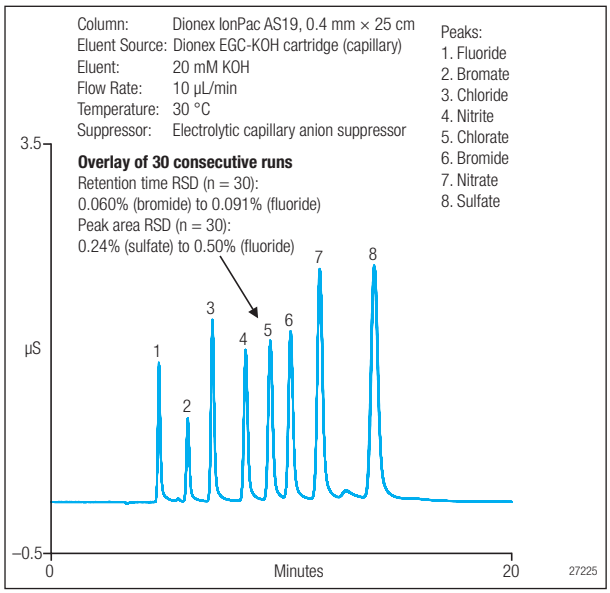


Figure 4. Isocratic separation of common anions obtained using a capillary Dionex IonPac AS19 column.

Figure 5 shows the gradient separation of a complex mixture of 22 anions on a capillary Dionex IonPac AS19 column at 10 µL/min. The results demonstrate that the Dionex ICS-5000 capillary RFIC system provides highly reproducible separation of target analytes under gradient elution conditions with retention time %RSD ranging from 0.09% (arsenate) to 0.18% (fluoride).

Figure 6 shows isocratic separation of common cations obtained using a capillary Dionex IonPac CS16 column. For 30 consecutive injections, the retention time RSD ranges from 0.052% (magnesium) to 0.092% (ammonium), and the peak area RSD ranges from 0.30% (potassium) to 0.46% (magnesium).

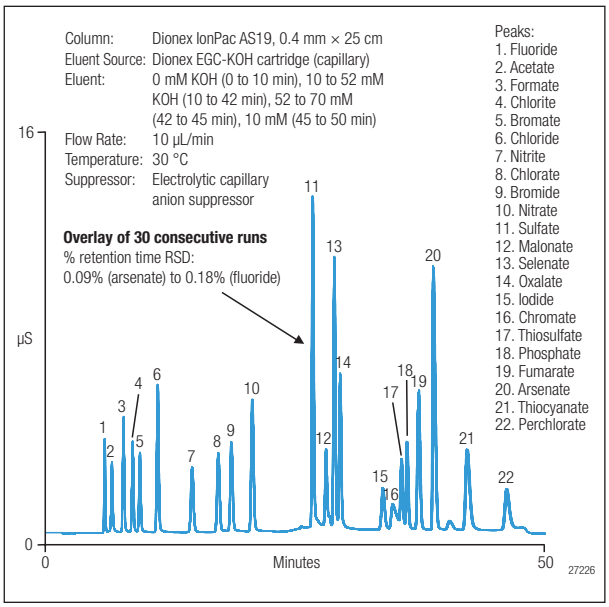


Figure 5. Gradient separation of 22 anions on a capillary Dionex IonPac AS19 column.

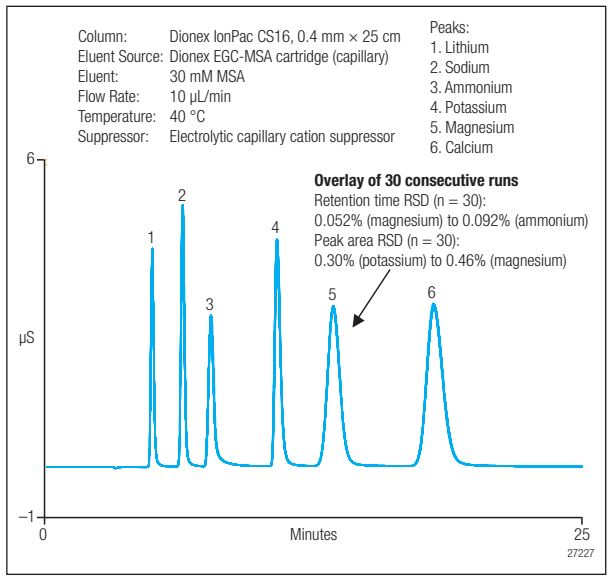


Figure 6. Separation of common cations obtained using a capillary Dionex IonPac CS16 column.

Figure 7 illustrates the determination of common anions in a treated wastewater sample using a Dionex ICS-5000 capillary RFIC system. In this study, a Dionex ICS-2000 conventional-scale RFIC system was used to analyze the same sample. The results demonstrate that the Dionex ICS-5000 capillary RFIC system provides analytical results equivalent to those used in the conventional-scale RFIC systems.

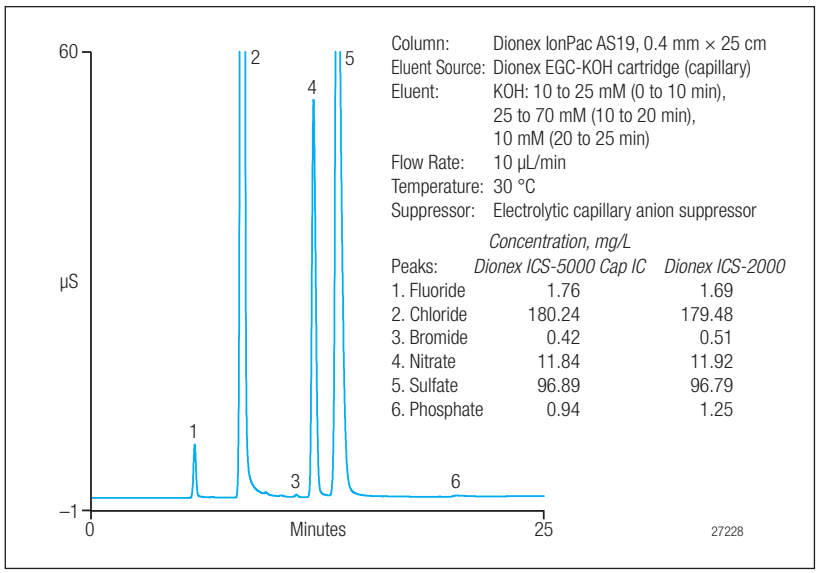
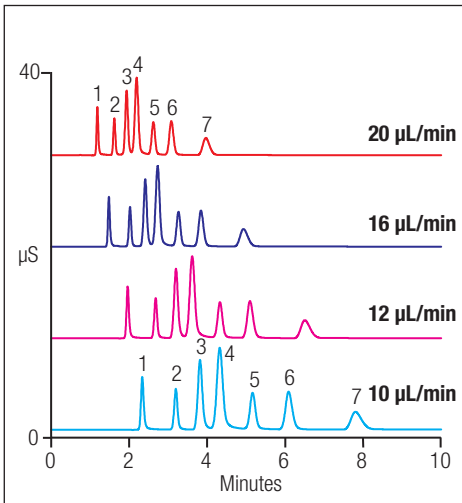


Figure 7. Determination of common anions in a treated wastewater sample.

The Dionex ICS-5000 capillary RFIC systems can be used to achieve fast separation of target analytes. Figure 8 shows the fast separation of seven common anions on a capillary Dionex IonPac AS18 column. By increasing the separation flow rate to 20 µL/min, the separation of seven common anions was obtained using 33 mM KOH as the eluent in less than 5 min. Figure 9 shows the fast separation of six common cations on a capillary Dionex IonPac CS12A column. In this example, the separation of cations was performed using 20 mM MSA and the separation flow rate was varied from 12 to 18 uL/min.
At 18 uL/min, the separation of six common cations was achieved in less than 6 min.



Column:	Dionex IonPac AS18-Fast, 0.4 mm × 15 cm
Eluent Source:	Dionex EGC-KOH cartridge (capillary)
Eluent:	33 mM KOH
Flow Rate:	10 to 20 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary anion suppressor

Peaks:	Retention Time at 20 µL/min (min)	Conc. (mg/L)
1. Fluoride	1.187	1.0
2. Chloride	1.623	1.5
3. Nitrite	1.937	5.0
4. Sulfate	2.197	7.5
5. Bromide	2.623	5.0
6. Nitrate	3.083	5.0
7. Phosphate	3.983	7.5

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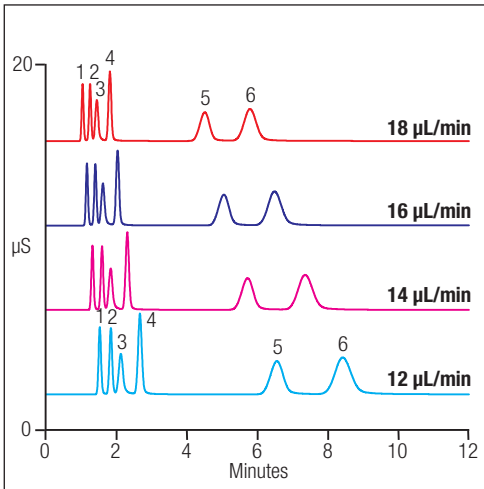
Figure 8. Fast separation of seven common anions on a capillary Dionex IonPac AS18 column.



Column:	Dionex IonPac CS12A-5µm, 0.4 mm × 15 cm
Eluent Source:	Dionex EGC-MSA cartridge (capillary)
Eluent:	20 mM MSA
Flow Rate:	12 to 18 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary cation suppressor

Peaks:	Retention Time at 18 µL/min (min)	Conc. (mg/L)
1. Lithium	1.037	0.5
2. Sodium	1.250	2.0
3. Ammonium	1.443	2.5
4. Potassium	1.813	5.0
5. Magnesium	4.507	2.5
6. Calcium	5.790	5.0

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Figure 9. Fast separation of six common cations on a capillary Dionex IonPac CS12A column.

Capillary RFIC systems provide improved determination of target analytes at trace levels since such measurements can be accomplished using relatively small volumes. It must be pointed out that a 10 µL injection onto a 0.4 mm i.d. column in a capillary IC system is equivalent to a 1000 µL injection onto a 4 mm i.d. column. Loading a 250 uL sample onto a capillary concentrator can be more conveniently accomplished than loading a 25 mL sample onto a conventional concentrator. Therefore, capillary IC systems can offer significant benefits in trace analysis, especially in applications where sample volumes are limited.

Figure 10 shows the separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS19 column. With a 10 µL injection, the Dionex ICS-5000 capillary RFIC system is capable of determining the target anions at concentrations ranging from 0.2 µg/L to 1.0 µg/L with excellent signal-to-noise ratios.

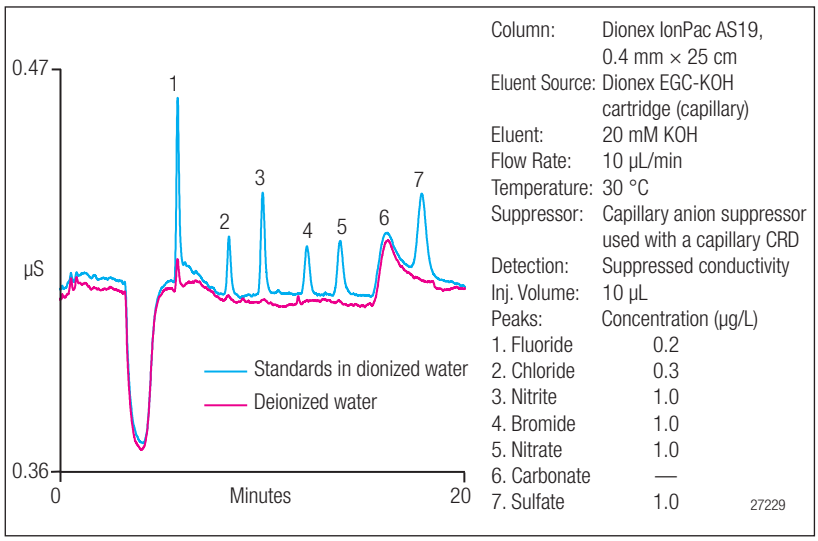

Figure 10. Separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS19 column with 10 µL injection.

Figure 11 shows the separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS15 column. In this example, 180 µL of a seven anion standard were loaded to a capillary concentrator using a Dionex AS autosampler. The results demonstrate that the Dionex ICS-5000 capillary RFIC system is capable of determining the target anions at concentrations ranging from 0.1 µg/L to 1.0 µg/L with excellent signal-to-noise ratios.

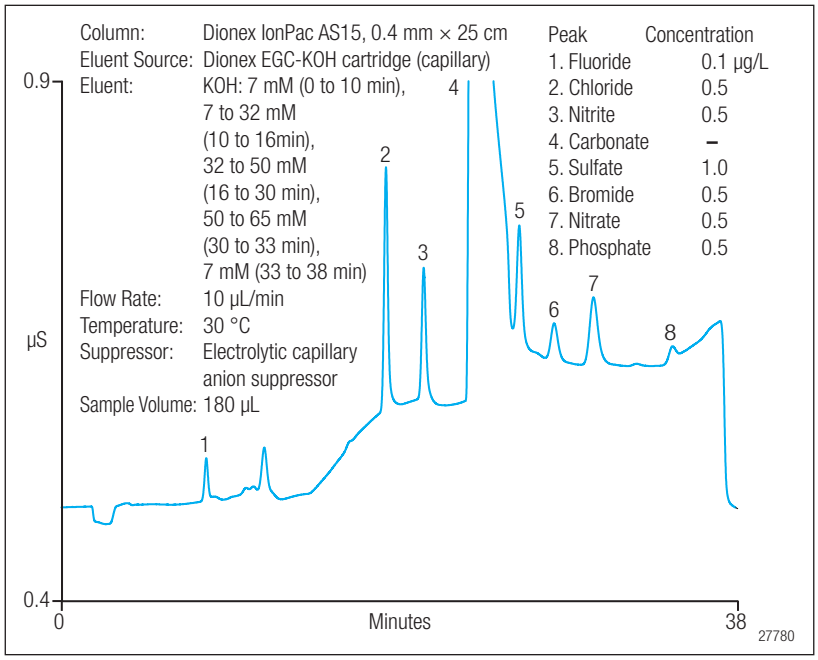

Figure 11. Separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS15 column with 180 µL injection.

The Dionex ICS-5000 capillary RFIC system using pulsed amperometric detector provides highly sensitive determination of carbohydrates. Figure 12 show the separation of six monosaccharides on a capillary Thermo Scientific™ Dionex™ CarboPac™ PA20 column using 10 mM KOH as eluent at 8 µL/min. The detection was performed using Au electrode using the standard carbohydrate quadruple waveform as well as the new PdH reference electrode. The system offers excellent reproducibility for separation of six monosaccharides. Over 10 consecutive injections, the retention time % RSD ranges from 0.04% (glucose) to 0.12% (fucose), and the peak area %RSD ranged from 0.71 (galactose) to 0.97% (galactosamine).

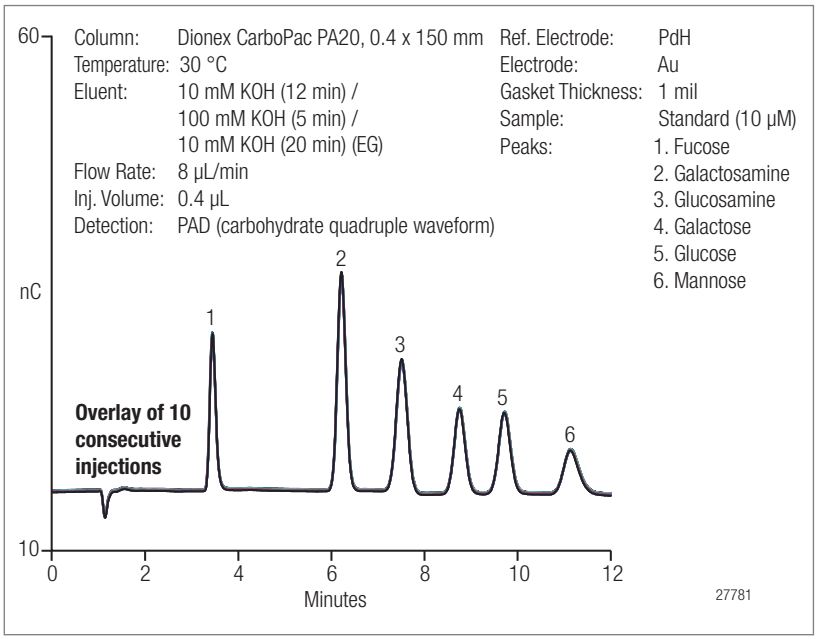

Figure 12. Separation of six monosaccharides.

The results shown in Table 2 indicate that the analytical performance of the capillary IC system with pulse amperometric detection for determination of carbohydrates is comparable to that of the analytical system. As shown in Figure 13 and Figure 14, the Dionex ICS-5000 capillary IC system with pulsed amperometric detection has been used successfully in the determination of carbohydrates in coffee and juice samples.

Table 2. Performance comparison of capillary and analytical systems: six monosaccharides.

	LOD (µM)		Linear Range (µM)		Correlation Coefficient	
	Capillary	Analytical	Capillary	Analytical	Capillary	Analytical
Fuc	0.024	0.023	0.024–50	0.023–20	0.9958	0.9932
GalN	0.018	0.014	0.018–25	0.014–20	0.9998	0.9920
GlcN	0.029	0.023	0.029–25	0.023–20	0.9949	0.9987
Gal	0.054	0.029	0.054–25	0.029–20	0.9964	0.9932
Glc	0.056	0.027	0.056–50	0.027–50	0.9986	0.9961
Man	0.068	0.059	0.068–50	0.059–50	0.9956	0.9975

Notes: 1. LOD: Limit of Detection; 2. Eluent: EG eluent (capillary); manually prepared eluent (analytical); 3. Injection volume: 0.4 µL (capillary); 25 µL (analytical).

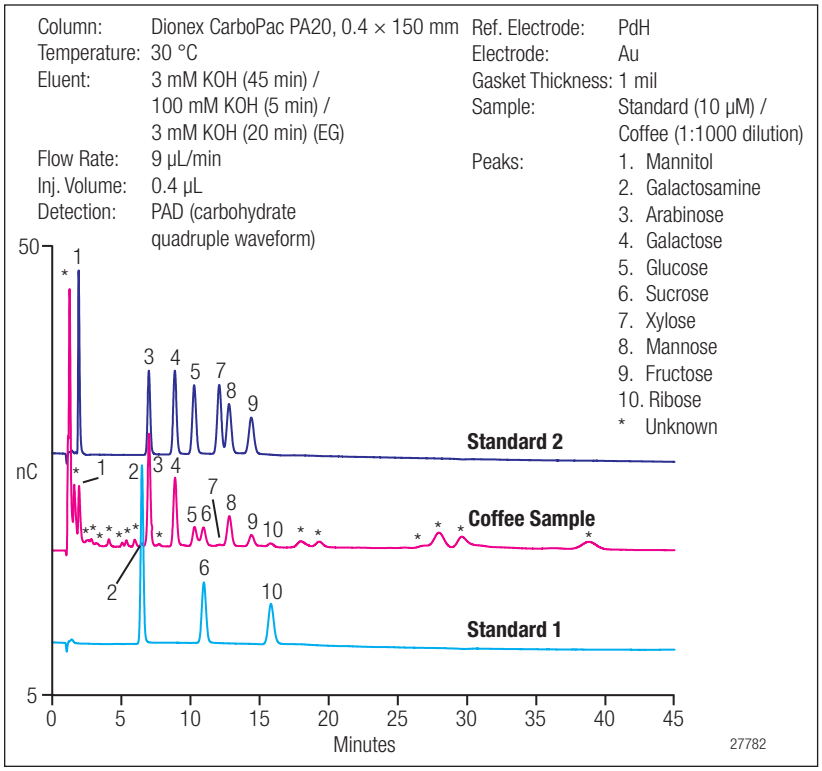

Figure 13. Separation of coffee sugars.

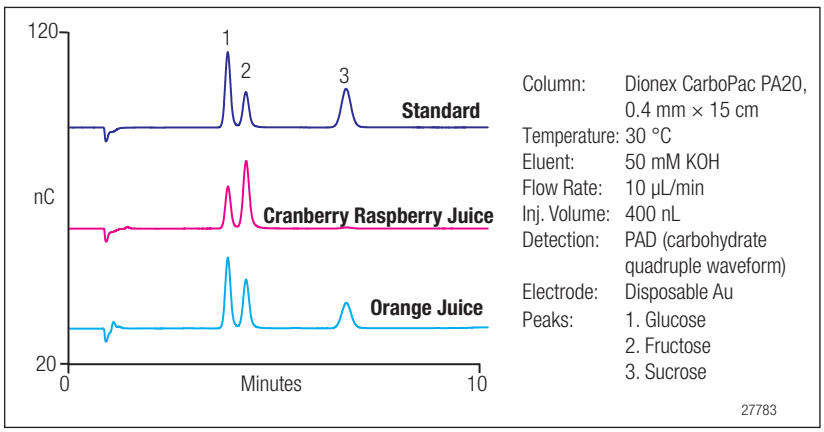

Figure 14. Separation of glucose, fructose, and sucrose in juice samples using a capillary RFIC system.

Conclusion

Dionex ICS-5000 capillary RFIC systems with on-line electrolytic eluent generation enable fast, highly reproducible isocratic and gradient IC separations. Capillary IC with suppressed conductivity detection allows determination of trace levels of ionic analytes. Capillary IC using a PdH reference electrode enables electrochemical detection of electroactive species with analytical performance comparable to that of conventional systems. Both conventional- and capillary-scale IC methods are supported on these versatile, convenient, and cost-effective systems.

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