New Developments in Capillary Ion Chromatography Systems with Electrochemical Detection and Their Applications

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Executive Summary

Capillary-scale IC offers substantial benefits over conventional IC, including higher mass sensitivity, improved separation efficiency and/or speed, smaller sample volumes, reduced eluent waste, and continuous system operation. Capillary IC systems with on-line electrolytic eluent generation and electrochemical detection enable highly reproducible and sensitive analysis of electroactive species. Cost-effective and convenient, this analytical approach is well suited for a range of applications, including the determination of low levels of saccharides in foods and beverages.

Key Words

Capillary IC, ICS-5000, Electrochemical detection, Saccharides, Food analysis

Abstract

There has been increasing interest in the development of capillary IC systems and methods for the determination of electrochemically active species. The practice of IC in the capillary format (i.e., using small-bore columns with internal diameters of <1 mm) has a number of potential advantages including small sampling volumes, potential of improved mass detection limits, and lower eluent consumption. Here, the use of such a system in carbohydrates analysis is presented. Low sample volumes, in particular, offer improved compatibility with bio IC applications, where biologically relevant samples are limited. Additionally, the operation of capillary IC at low flow rates reduces waste generated in the laboratory setting. The practice of IC in the capillary format offers possibilities of new selectivity for difficult applications using new columns packed with previously difficult-to-prepare stationary phases.

Here, ongoing efforts in the development of capillary IC systems with on-line electrolytic eluent generation (EG) and electrochemical detection for determination of target analytes are reported. A discussion is presented on the optimization of capillary consumables and the advantages of using capillary IC systems in the determination of target analytes. Furthermore, it is also demonstrated that with Always on, Always Ready, a system at capillary chemistries and flow rates allows undiminished sensitivity and selectivity with minimum involvement by the IC user.

Introduction

Ion chromatography is a prominent technique to determine inorganic and organic ions in all kinds of liquid matrices. Monitoring ions in drinking, surface, waste, and process waters is routinely done using IC with either laboratory or process IC systems. Common applications include testing of disinfectant byproducts such as bromate in tap or bottled water, iodide and iodate in sea water, amines in wastewater, and trace-level anions and cations in ultrapure water for the semiconductor and power industry. It is important to determine the type and composition of carbohydrates in food, beverage, and dairy samples. Moreover, monosaccharide composition analysis is a powerful tool in the characterization of glycoproteins. The results are useful in glycoprotein drug development. Most of these applications are performed using column chemistries in 3 or 4 mm i.d. format and flow rates of 0.50–1 mL/min.

Here, the authors present the next evolution in IC using capillary chemistries. Capillary chemistries use 0.4 mm i.d. columns at flow rates of 10 µL/min. This allows an IC system to be operated continuously for up to 12 months with only 5.2 L of water. Furthermore, less time is required for eluent preparation and equilibration or calibration because the system can be always ready for the next sample. Due to the low eluent consumption, the waste generated is also reduced, which makes capillary IC beneficial when toxic or radioactive samples are analyzed. Also, the injection volume is reduced to 400 nL typically while maintaining minimum detection limits. This makes capillary IC suitable for applications that are sample-limited, such as metabolomics, corrosion monitoring of individual corrosion spots, and process monitoring of small-scale reactors.

The Thermo Scientific™ Dionex™ ICS-5000 system is the first IC system that supports analytical scales (4 and 2 mm) and capillary chemistries (Figure 1). The dual system allows users to operate one channel with 2 or 4 mm column chemistries and explore capillary chemistries on the other channel. The Dionex ICS-5000 system supports manually prepared eluents as well as Reagent-Free™ IC (RFIC™) technologies on analytical and capillary scales, and eluent regeneration for 4 mm column chemistries (Figure 2).

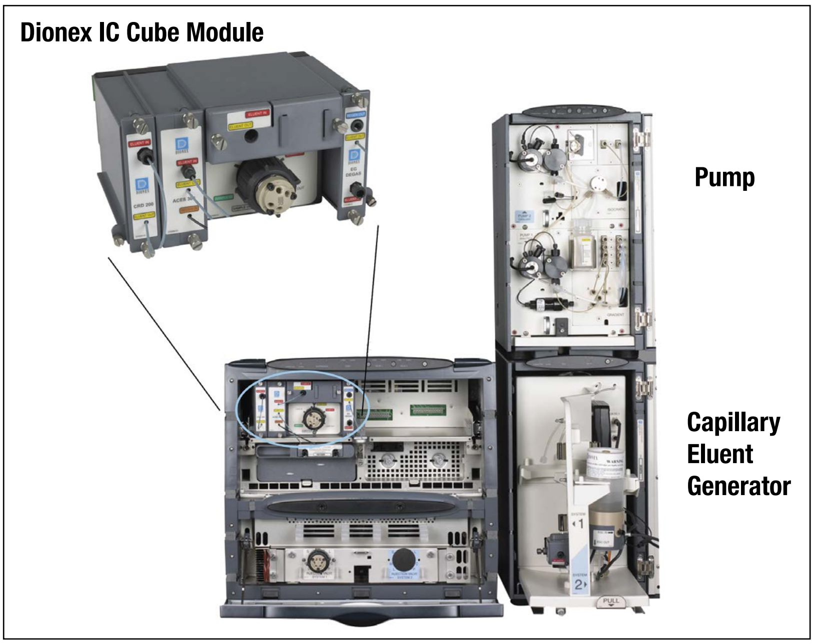


Figure 1. Dionex ICS-5000 system with Thermo Scientific™ Dionex™ IC Cube™ module.

The specifications of the Dionex ICS-5000 system are listed below.

Features	ICS-5000 System
Detector Compartment Temperature zones	**Dual Zone** Lower zone has one temperature; both cubes have independent temperature settings
Suppressors Capacity Void volumes	**Anion Capillary Electrolytic Suppressor** 2 µeq/min <1.0 µL
Pump Technology Pump flow rates Typical flow rates Maximum pressure Pressure ripple Flow accuracy	**Dual-Piston (in series)** 0.001– 3.000 mL/min 5–20 µL 6000 psi (capillary flow rates) <0.25% at 10 µL/min <0.1%
Detection Technology Cell volume (at working electrode) Reference electrode Noise specification	**Electrochemical Detector** <130 nL Palladium hydrogen <10 pA or 20 pC
Eluent Generation Concentration range Lifeline	**RFIC-EG** 0.1–200 mM (capillary) 18 months continuous operation (75 mM at 10 µL/min)

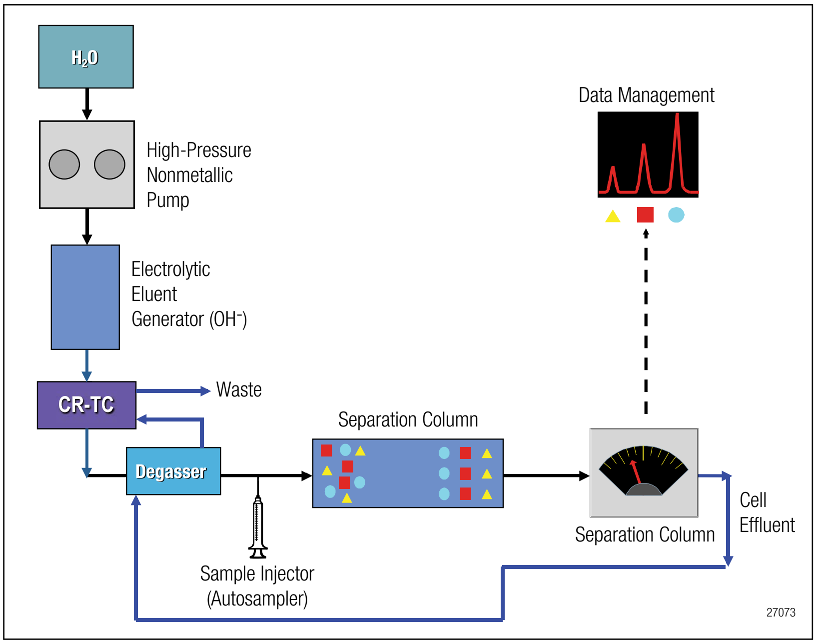


Figure 2. Block diagram of a capillary RFIC system with electrochemical detection.

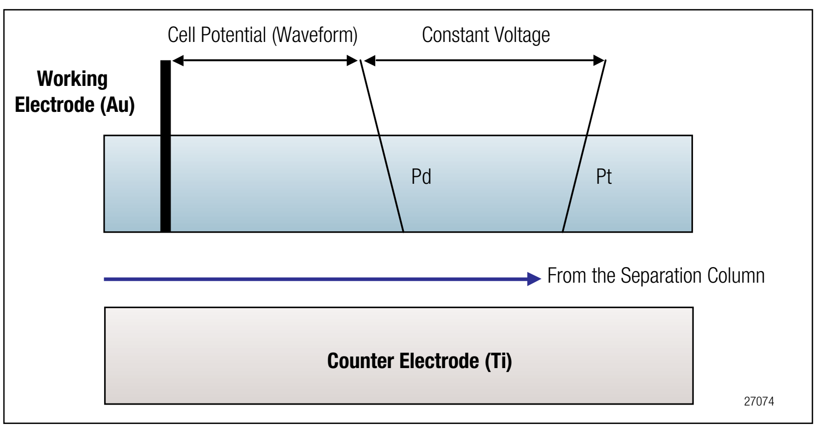
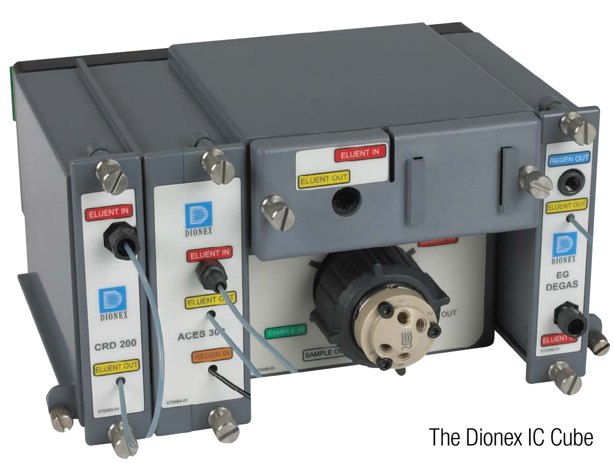


Figure 3. PdH reference electrode.

System Integration With the Dionex IC Cube

In liquid chromatography, often smaller i.d. columns and especially nano and capillary columns are difficult to use. Operators need to be careful in making fluidic connections and ensuring that they are dead-volume free. In addition, all components need to be volume optimized for low flow rates of 10 µL/min. In capillary-scale, a dead-volume of several nanoliters can broaden peaks and dramatically affect the chromatographic resolution. To overcome these issues, the Dionex ICS-5000 system has all capillary consumables in a separate compartment called the Dionex IC Cube module. The Dionex IC Cube module houses the capillary column and guard column in a cartridge, the injection valve with an internal loop of 400 nL, the capillary suppressor module, an optional carbonate removal device, and the eluent generator degasser module. The usage of cartridges simplifies the plumbing by reducing the number of fluidic connections by 50% compared to the same analytical configuration.



The Dionex IC Cube

Results

The newly designed, capillary-based Dionex ICS-5000 system was used to detect monosaccharides in various matrices, including orange and cranberry-rasberry juice (Figures 4–8). The system was initially qualified with a mix of six monosaccharides and limits of detection (LOD) were determined (see Table 1).

After completing the initial runs on six monosaccharides, alditol, and disacchardides, the Dionex ICS-5000 system was used to determine glucose, fructose, and sucrose in two fruit juices to evaluate the system with real-world samples (matrices).

Table 1. Analytical performance: six monosaccharides.

	LOD (µM)	Linear Range (µM)	Correlation Coefficient
Fuc	0.024	0.024–50	0.9958
GalN	0.018	0.018–25	0.9998
GlcN	0.029	0.029–25	0.9949
Gal	0.054	0.054–25	0.9964
Glc	0.056	0.056–50	0.9986
Man	0.068	0.068–50	0.9956

Note: Limit of detection (LOD) is three times the noise; injection volume is 400 nL.

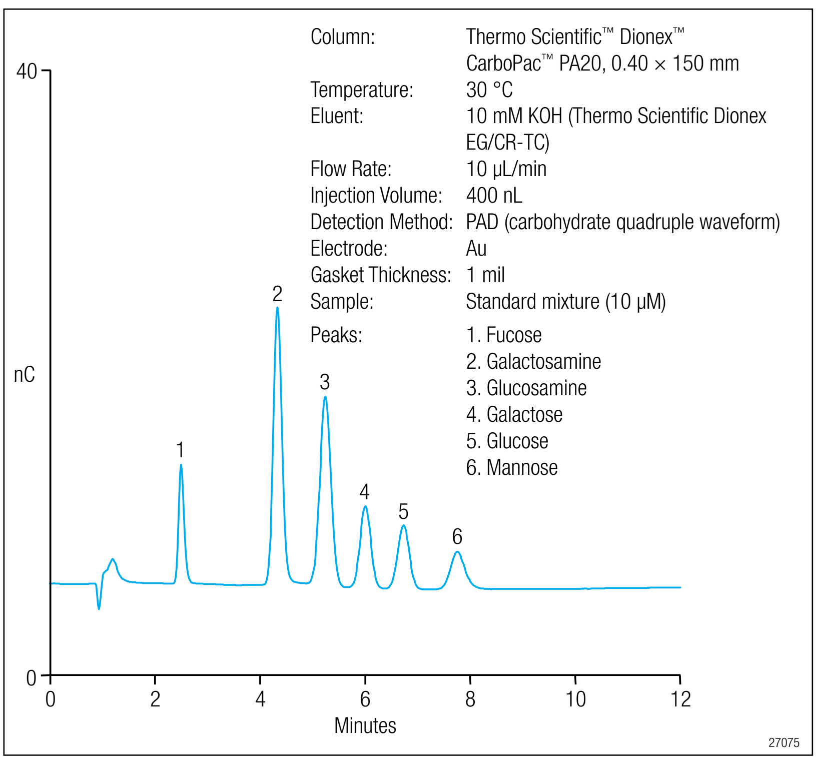
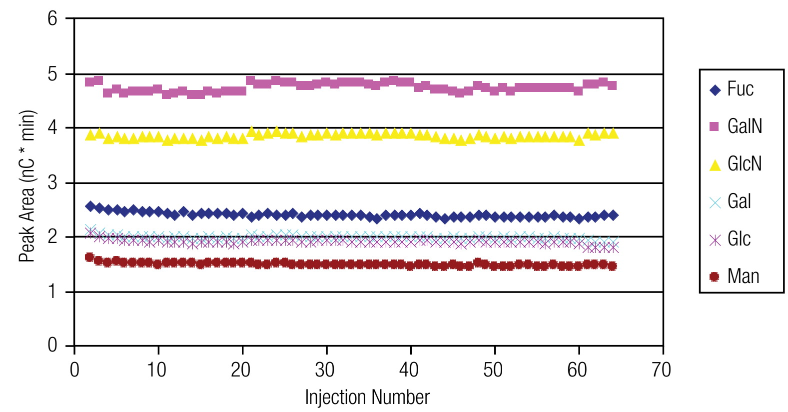


Figure 4. Separation of six monosaccharides.



	Fuc	GalN	GlcN	Gal	Glc	Man
Area RSD (%)	1.87	1.63	1.15	1.66	2.10	1.91

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Figure 5. Two-day detection stability of six monosaccharides.

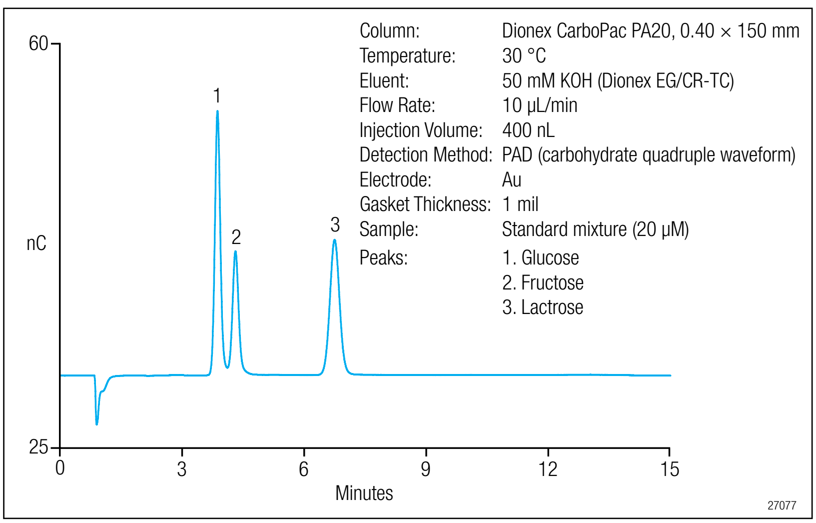

Figure 6. Separation of mono- and disaccharides.

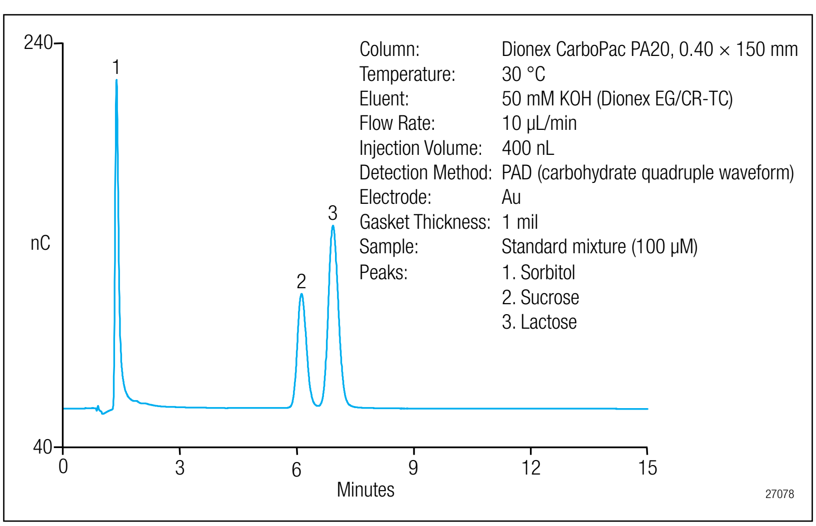

Figure 7. Separation of alditol and disaccharides.

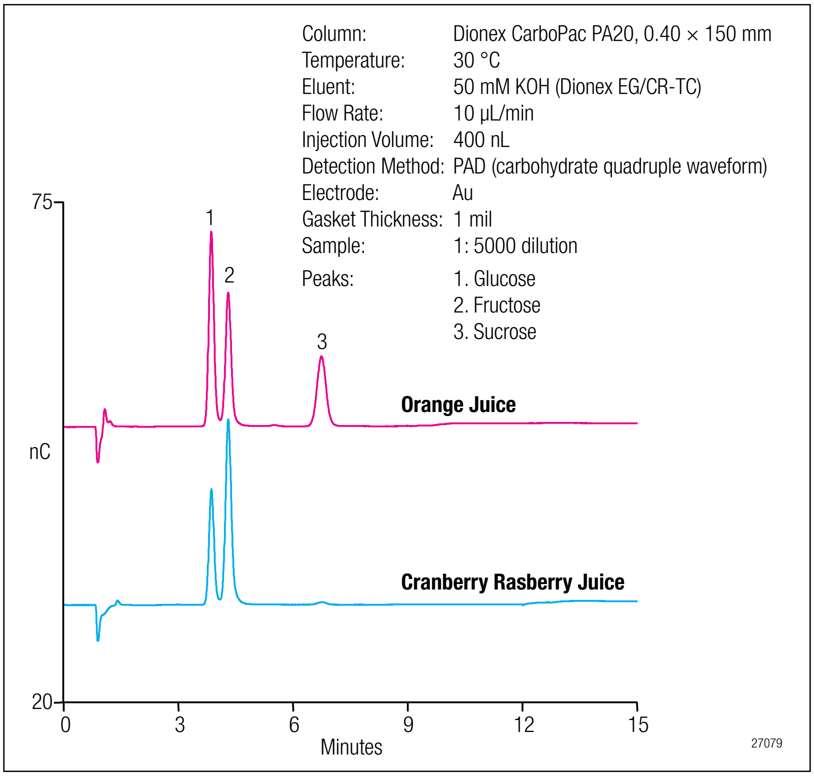

Figure 8. Analysis of fruit juice samples.

Conclusion

Capillary IC with electrochemical detection using the Dionex ICS-5000 system enables reproducible separation and sensitive detection of alditols, mono-, and disaccharides. Advantages of this platform include minimal eluent consumption (<15 mL/day), improved detection limits for monosaccharides (<10–70 nM), and small sample sizes (400 nL injection volumes).

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