

# New Developments in Capillary Ion Chromatography using 4 $\mu\text{m}$ Columns and Charge Detection

Barbara Shao, Terri Christison, Fei Pang, Cathy Tanner, and Frank Hoefler  
Thermo Fisher Scientific, Sunnyvale, CA, USA

## Executive Summary

Capillary IC offers substantial benefits over conventional IC, including higher mass sensitivity, improved separation efficiency and/or speed, smaller sample volumes, reduced eluent consumption, improved MS compatibility, and continuous system operation. High-pressure capillary IC using 4  $\mu\text{m}$ -particle-size columns enables higher efficiency separations of complex samples and allow faster analysis. Charge detection allows determination of all ionic analytes and provides a complementary technique to suppressed conductivity detection for analysis of ionic compounds.

## Key Words

Capillary IC, High pressure IC, Charge detection, IonPac

## Overview

**Purpose:** New solutions highlighting the applications and benefits of high-pressure capillary ion chromatography with 4  $\mu\text{m}$ -particle-size columns in a compact, integrated IC system are discussed. Furthermore, the benefits of a Reagent-Free™ IC (RFIC™) system with eluent generation capabilities to achieve consistent results, day-to-day, instrument-to-instrument, and operator-to-operator are presented. Advantages of suppressed conductivity with charge detection (QD) are demonstrated.

**Methods:** All applications were developed on an integrated, high-pressure Thermo Scientific™ Dionex™ ICS-4000 Capillary HPIC system using capillary Thermo Scientific™ Dionex™ IonPac™ 4  $\mu\text{m}$ -particle-size columns. Suppressed conductivity and the new charge detectors were used in series. Eluents were electrolytically generated, using the RFIC system capabilities of the Dionex ICS-4000 HPIC system.

**Results:** Fast separations of biogenic amines using capillary high-pressure IC (HPIC) are achieved in less than 9 min. High-resolution separations of inorganic anions and organic acids are presented using 4  $\mu\text{m}$ -particle-size columns. More peaks can be detected in orange juice with the new charge detector.

## Capillary Ion Chromatography

IC has become one of the preferred technologies for determining ionic analytes in any type of matrix, from ultrahigh purity water, to drinking and wastewater, to fruit juices and bodily fluids. Recent developments in ion chromatography, including capillary IC, which was introduced with the Dionex ICS-5000 system, have generated great interest. In 2012, the first dedicated capillary HPIC system was introduced, targeting routine analysis. In capillary IC, packed columns with internal diameters of 0.4 mm are typically used at flow rates of 10  $\mu\text{L}/\text{min}$ , thus enabling continuous operation with less than 15 mL of mobile phase per day or 5.25 L per year.

<b>Format</b>	Standard bore	Capillary
<b>Column i.d.</b>	4 mm	0.4 mm
<b>Typical Flow Rate</b>	1.0 mL/min	10 $\mu$ L/min
<b>Typical Injection Volume</b>	25 $\mu$ L	0.4 $\mu$ L
<b>Eluent Consumption/ Waste Generation</b>	43.2 L/month	0.432 L/month
<b>ECG Lifetime (at 75 mM)</b>	28 days	18 months
<b>Mass Detection Limits</b>	7000 fg	70 fg

Further advantages include:

- Less sample volume is required due to increased mass sensitivity. This is important for sample limited applications, e.g., the analysis of ions in biological fluids.
- The low flow rates are beneficial for interfacing with mass spectrometry, providing increased sensitivity for trace level analysis.
- Two-dimensional separations using a 4 mm-inner-diameter column in the first dimension and a capillary column in the second dimension allow ng/L (ppt) level detection with only 1 mL of sample and suppressed conductivity detection.

Capillary IC was built with technologies currently available for standard and microbore IC, including RFIC with eluent generation, electrolytic suppression with conductivity detection, and electrochemical detection. Capillary IC also utilizes new technologies such as charge detection, high-pressure eluent generation, and the use of high efficiency 4  $\mu$ m-particle-size columns.

## Methods

### Sample Preparation

Typical sample preparation includes dilution and filtration using 0.45  $\mu$ m nylon membrane filters.

### Ion Chromatography

#### Equipment and Data Analysis

Dionex ICS-4000 Capillary HPIC system consisting of a capillary pump; an Eluent Generator module (EG); a Thermo Scientific™ Dionex™ IC Cube™ housing the 0.4  $\mu$ L injection valve and all capillary consumables; a conductivity (CD), electrochemical (ED), or charge detector (QD); and a Dionex AS-AP autosampler.

Thermo Scientific™ Dionex™ Chromeleon™ 6.8 Chromatography Data System software, was used for instrument control and data analysis and management.

#### Conditions

The conditions are included in the figures.

### High-Pressure Ion Chromatography

Capillary HPIC systems allow continuous operation with eluent generation at pressures up to 34 MPa (5000 psi). To extend the pressure range from 3000 to 5000 psi requires the use of HPIC components, including the pump heads, eluent generation cartridge, and the eluent generation degasser. This enables the use of 4  $\mu$ m-particle-size columns, which produce higher backpressures under standard conditions. The advantages of these new columns include:

- Smaller particle diameter = higher chromatographic efficiency
- Higher chromatographic efficiency =
  - faster separations at higher flow rates without sacrificing resolution
  - or
  - higher resolution at standard flow rates

Figure 1 shows an example for a fast separation of inorganic cations and biogenic amines in less than 9 min. All peaks are baseline resolved due to the high efficiency of this column. To achieve these fast run times, the flow rate was increased from the standard of 0.010 mL/min to 0.020 mL/min and a steep gradient was applied. Examples for high-resolution separations are shown in Figure 4.

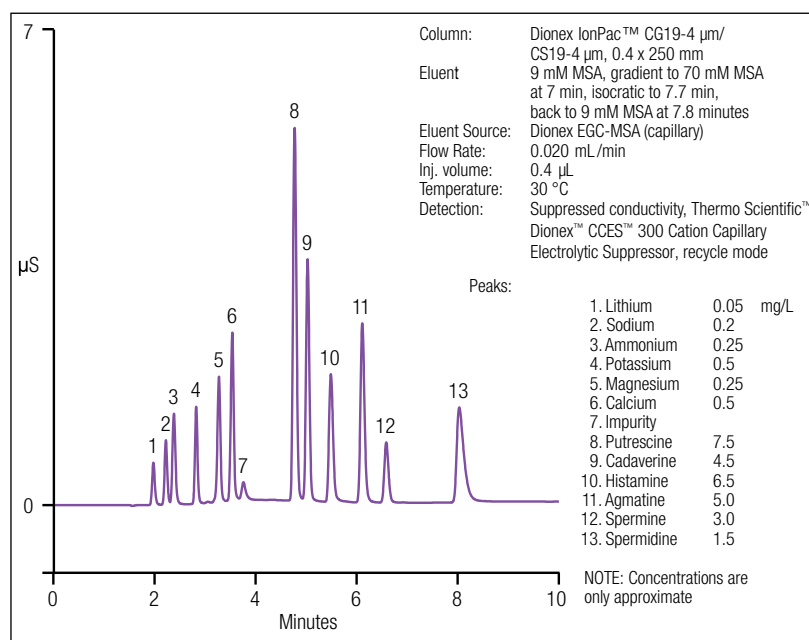


Figure 1. Fast separation of nine inorganic cations and biogenic amines.

### Principle of Charge Detection

The charge detector uses two membranes, an anion and a cation exchange, to separate the eluent channel from two detector channels. The anode and cathode are located in the two detector channels. A constant voltage is applied to the electrodes, causing ions to migrate from the eluent channel through the membrane into the detector channels (Figure 2). When ions reach the electrodes, a current proportional to the charges is generated. The resulting response is similar for the same number (molarity) of similarly charged ions independent from the degree of dissociation, thus providing universal response. Therefore, the charge detector signal is twice as strong for doubly and three times as high for triply charged ions, e.g., phosphate (Figure 5).

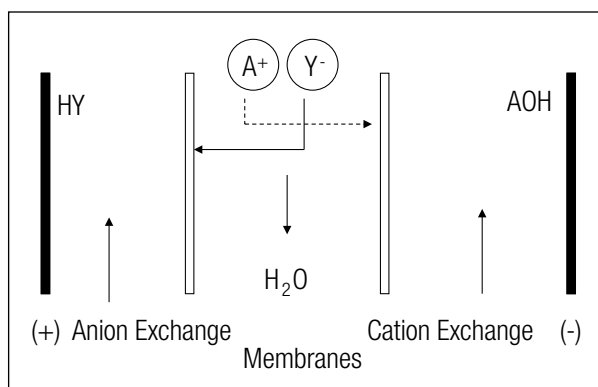


Figure 2. Schematic of a charge detector cell.

The charge detector responds to all ionic compounds and therefore is best used with hydroxide-based eluents for anion analysis or with methanesulfonic acid eluents for cation analysis, as a second detector installed in series with a suppressed conductivity detector. The charge detector removes all ions from the eluent stream and is therefore always installed last in series with other detectors. A typical setup is shown in Figures 3 and 4.

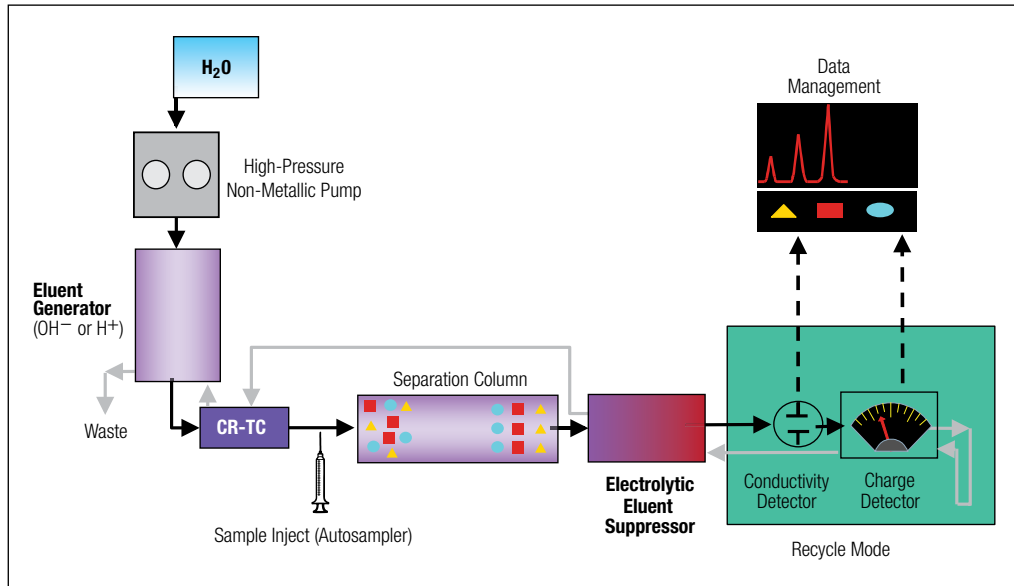


Figure 3. Schematic setup of a capillary RFIC system with suppressed conductivity detection and charge detection.

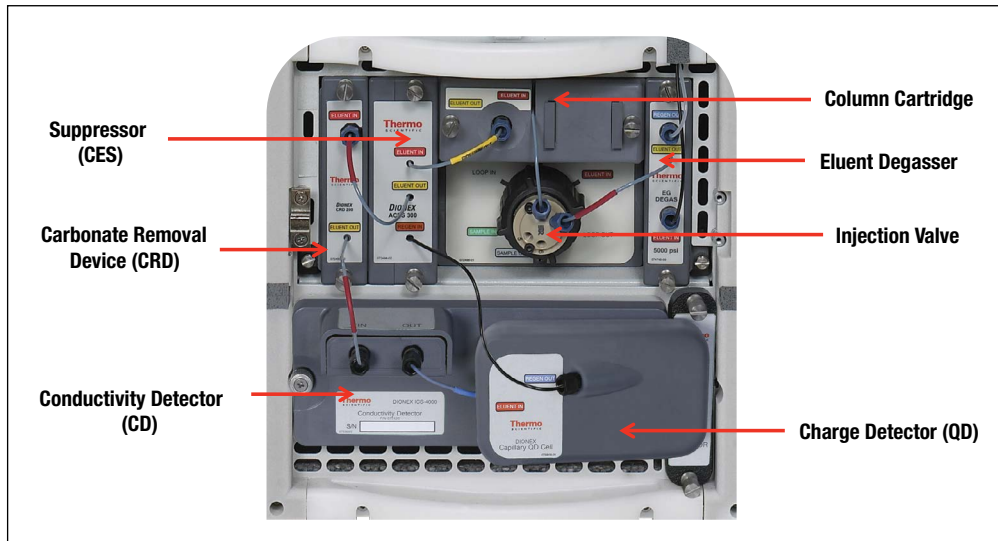


Figure 4. Capillary components in a Dionex ICS-4000 Capillary HPIC system.

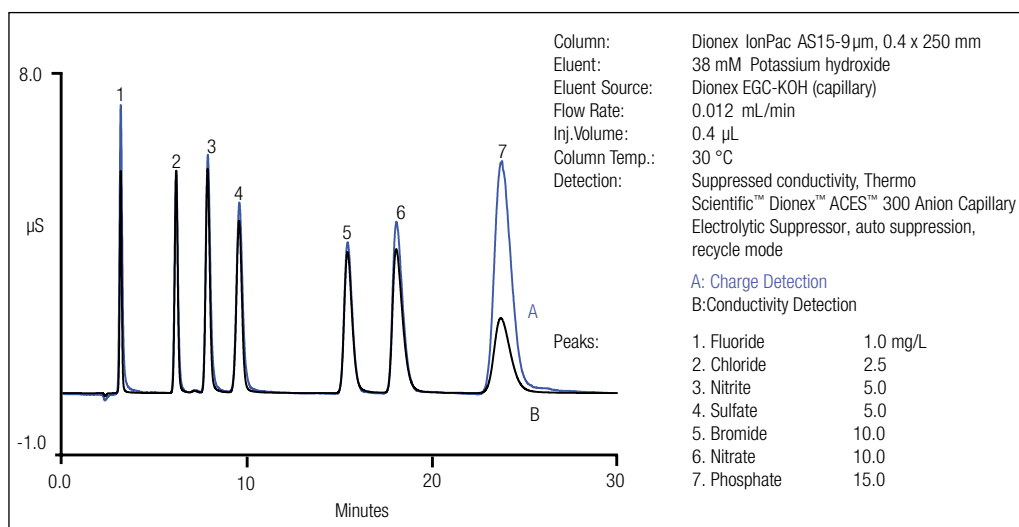


Figure 5. Overlaid chromatograms of a seven anion standard, obtained with suppressed conductivity detection and charge detection.

### Analysis of Organic Acids and Inorganic Ions in Orange Juice

The separation of organic acids and inorganic ions in an orange juice sample demonstrates the high efficiency of the Dionex IonPac AS11-HC-4µm capillary column (Figure 6). Only 0.4 µL of a 1:50 diluted, filtered sample was injected onto the column. The black trace shows the chromatogram obtained with suppressed conductivity detection and the blue trace represents the one with charge detection. The two chromatograms are scaled to the chloride peak. This example demonstrates that weakly dissociated ions such as organic acids, acetate and maleate, as well as multi-valent ions phosphate and citrate show significantly higher response with charge detection.

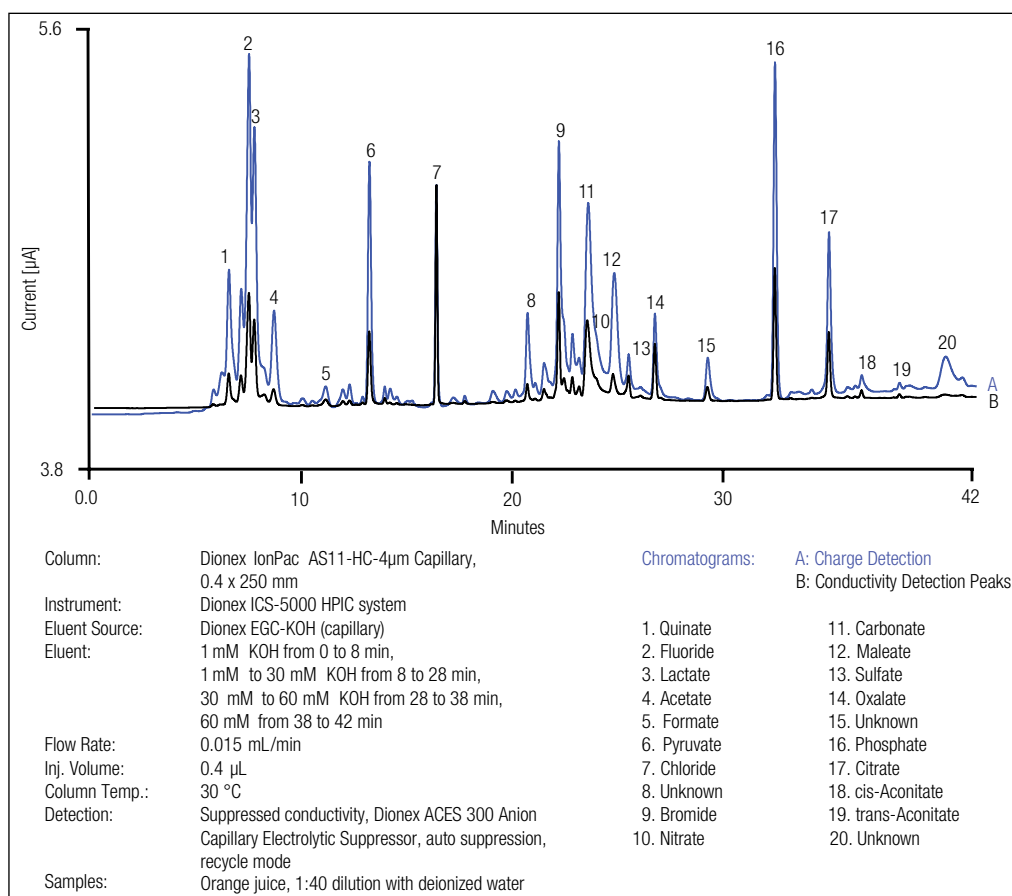


Figure 6. Determination of organic acids and inorganic anions in orange juice using a Dionex IonPac AS11-HC-4µm, 0.4 x 250 mm, anion-exchange column with suppressed conductivity and charge detections.

## Conclusion

High pressure IC with 4 µm-particle-size columns enables high chromatographic resolution or fast analysis, and is ideal for operation at higher flow rates due to the low eluent consumption. In addition, charge detection provides more information, universal detection, and similar response for weakly and strongly dissociated ions.

## References

For more information regarding the Dionex ICS-4000 HPIC system, charge detection, and Dionex IonPac CS19-4µm and AS11-HC-4µm columns, refer to the following.

1. Thermo Scientific Dionex ICS-4000 with Charge Detection, <http://www.dionex.com/en-us/products/ion-chromatography/ic-rfic-systems/ics-4000/lp-111672.html>.
2. Dionex (now part of Thermo Scientific) Application Note 143, *Determination of Organic Acids in Fruit Juices*.
3. Thermo Scientific Dionex IonPac CS19-4µm Cation-Exchange Column, <http://www.dionex.com/en-us/products/columns/ic-rfic/cation-packed/ionpac-cs19-4um/lp-111500.html>.
4. Thermo Scientific Dionex IonPac AS11-HC Hydroxide-Selective Anion-Exchange Column, <http://www.dionex.com/en-us/products/columns/ic-rfic/hydroxide-selective-packed/ionpac-as11hc/lp-73257.html>.

## [www.thermofisher.com/dionex](http://www.thermofisher.com/dionex)

©2016 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

**Australia** +61 3 9757 4486  
**Austria** +43 1 616 51 25  
**Benelux** +31 20 683 9768  
 +32 3 353 42 94  
**Brazil** +55 11 3731 5140

**China** +852 2428 3282  
**Denmark** +45 36 36 90 90  
**France** +33 1 39 30 01 10  
**Germany** +49 6126 991 0  
**India** +91 22 2764 2735

**Ireland** +353 1 644 0064  
**Italy** +39 02 51 62 1267  
**Japan** +81 6 6885 1213  
**Korea** +82 2 3420 8600  
**Singapore** +65 6289 1190  
**Sweden** +46 8 473 3380

**Switzerland** +41 62 205 9966  
**Taiwan** +886 2 8751 6655  
**UK** +44 1276 691722  
**USA and Canada** +847 295 7500

**Thermo**  
 S C I E N T I F I C

Part of Thermo Fisher Scientific