

# Determinations of Inorganic Anions and Organic Acids in Beverages Using Suppressed Conductivity and Charge Detection

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## Overview

**Purpose:** To demonstrate the advantages of using dual CD and QD Charge detectors in series for Ion Chromatography (IC).

**Methods:** Inorganic anions and organic acids were separated on a high-capacity 4- $\mu\text{m}$  particle Thermo Scientific™ Dionex™ IonPac™ AS11-HC-4 $\mu\text{m}$  capillary column and detected with suppressed conductivity in series with charge detection. Analysis was facilitated by a high-pressure capillary IC system.

**Results:** Very high efficient separations at > 3500 psi system pressures were demonstrated on the Dionex IonPac AS11-HC-4 $\mu\text{m}$  on a dedicated capillary IC system. The QD charge detector shows comparably higher charge response for organic acids than for chloride and sulfate and can detect other peaks previously not detected by conductivity (CD). The responses by the different detectors were used to assess peak purity, thereby improving reporting accuracy.

## Introduction

Determinations of organic acid profiles in fruit juices are important in the beverage industry to ascertain product quality and to meet labeling requirements for food products. Ion chromatography with suppressed conductivity is the ideal analytical method for ionic analytes. However organic acids which are weakly ionized can exhibit lower conductivity responses versus concentration than strongly ionized anions, such as chloride and sulfate. However, the new Thermo Scientific Dionex QD Charge Detector promotes complete dissociation of even weakly ionized compounds.

## Methods

### Samples and Sample Preparation

Commercial juice samples were diluted and filtered (0.2  $\mu\text{m}$ ) with a syringe filter.

### Ion Chromatography Instrumentation

Thermo Scientific™ Dionex™ ICS-4000 Capillary HPIC™ system with

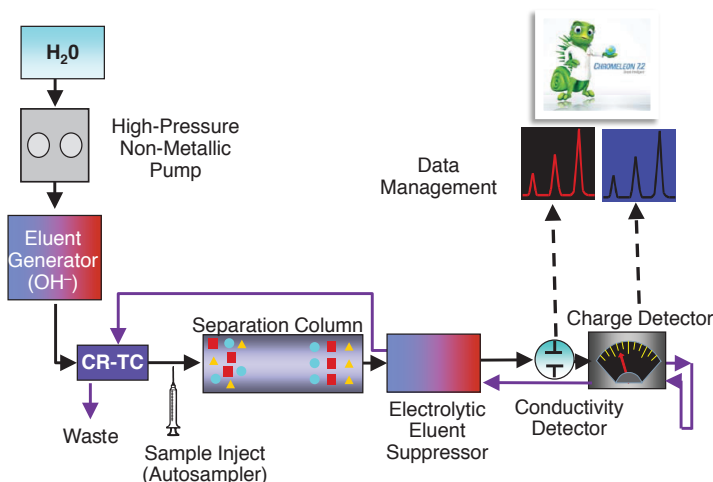
- Thermo Scientific Dionex IonPac ATC-500 trap column
- Thermo Scientific™ Dionex™ IC Cube™ column and consumables module
- Thermo Scientific Dionex CD Conductivity Detector
- Thermo Scientific Dionex QD Charge Detector
- Thermo Scientific Dionex QDC 300 Charge Detector Cell
- Thermo Scientific Dionex AS-AP Autosampler

The flow diagram is shown in Figure 1.

**TABLE 1. IC Conditions for Beverage Analysis**

Column set:	Dionex IonPac AS11-HC-4 $\mu\text{m}$ , guard and separation columns, 0.4 mm
Eluent Source:	Thermo Scientific Dionex EGC-KOH capillary cartridge with Thermo Scientific Dionex CR-ATC capillary trap column
Gradient:	Potassium hydroxide, listed in figures.
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 $\mu\text{L}$
Column Temp.:	30 °C
Detection:	A: Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle mode, Thermo Scientific Dionex CRD 180 Carbonate Removal Device
	B: QD Charge Detection, Dionex QDC 300 cell, 6 V, recycle mode.

**FIGURE 1. Flow diagram of the capillary IC system with suppressed conductivity and charge detection.**



The high-pressure Dionex ICS-4000 HPIC system is an integrated single channel system designed for capillary ( $\mu\text{L}/\text{min}$ ) flow rates with all of the advantages of high pressure capillary IC while requiring less analytical bench space (Figure 2A). For the first time in a compact design, this IC has the flexibility to support conductivity, or conductivity with charge detection (Figure 2B and 2C), or electrochemical detection.

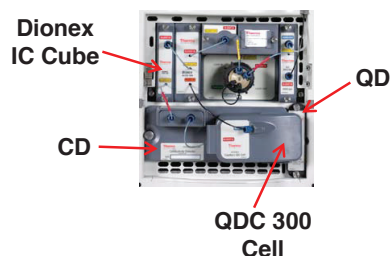
**FIGURE 2. Dionex ICS-4000 HPIC dedicated capillary system with the doors open and the “hood” up.**



**FIGURE 2A. Dionex ICS-4000 HPIC System**



**FIGURE 2B. Dionex QDC 300 Cell**



**FIGURE 2C. Dionex QDC 300 Cell Installed**

### Data Analysis

Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software

## Results

### Method

Anions are separated by anion-exchange chromatography using electrolytically generated potassium hydroxide gradient at  $\mu\text{L}/\text{min}$  on a high-capacity,  $4\ \mu\text{m}$  resin particle IonPac AS11HC- $4\ \mu\text{m}$  capillary IC column. This column was optimized for high resolution separations of organic acids with inorganic anions. As the anions eluted from the column, the anions were detected by suppressed conductivity and then charge detection. The instrument and data processing were managed by Chromeleon data systems software.

# Results

## QD Charge Detection

A charge detector (QD) is a constant voltage membrane device that maintains a specified potential at the anode and cathode (Figure 3).<sup>1</sup> As the sample passes through the detector, the ions are drawn through the ion-exchange membranes, drawing a current to balance the charge. This results in a response proportional to the charge state and a significantly higher response for weakly ionized compounds than would be obtained with CD.

FIGURE 3. Mechanisms of Dionex Charge Detection.

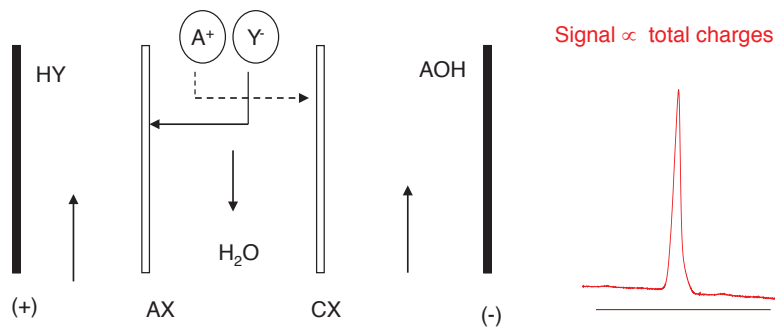


Figure 4 shows increased linear response for weakly ionized analytes with charge detection.<sup>1</sup>

FIGURE 4. Compares CD (A) and QD (B) responses with concentration.

FIGURE 4A.

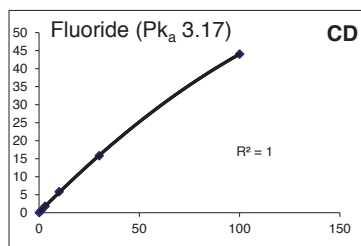
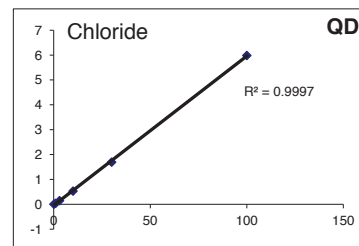
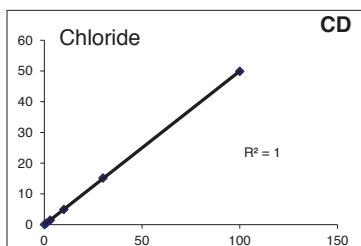
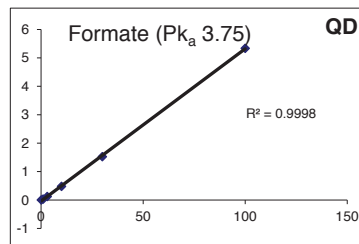
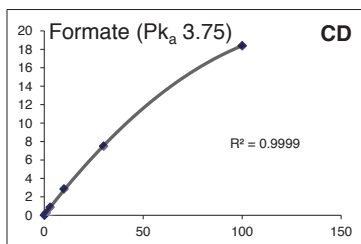
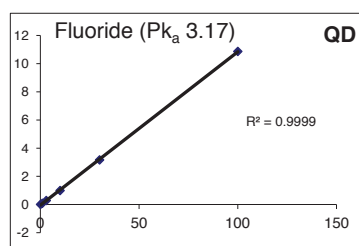


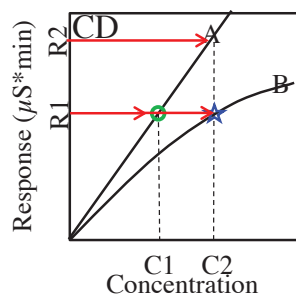
FIGURE 4B.



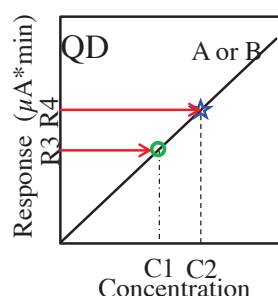
Figures 5 and 6 show advantages of using different detectors with different responses. In Figure 5A, the same conductivity response R1 results in concluding C1 concentration for the **green circle** but ambiguous results R1 and R2 for the **blue star**. This is clarified by the distinct response by QD detection (Figure 5B). In Figure 6B, the **red circle** and **blue star** have the same QD response per concentration but can be differentiated by their different conductivity responses (Figure 6A).

**FIGURES 5–6. Conductivity Detection Combined with Charge Detection Clarifies Ambiguous Quantitative Determinations.**

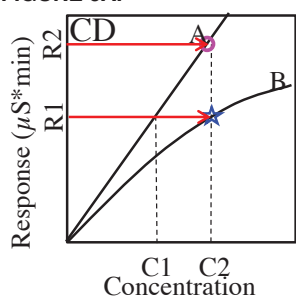
**FIGURE 5A.**



**FIGURE 5B.**



**FIGURE 6A.**



**FIGURE 6B.**

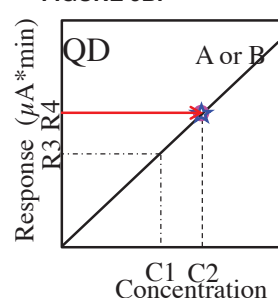


Figure 7 shows the QD chromatogram normalized at the chloride peak and overlaid on the CD chromatogram of a diluted guava juice sample.<sup>2</sup> The chromatograms show a higher proportional charge with QD than CD for organic acids in diluted guava juice.

**FIGURE 7. Comparison of QD to CD responses in diluted guava juice.**

Columns:	Dionex IonPac AS11-HC-4 $\mu$ m column set, 0.4 mm	Detection:	A: Suppressed conductivity, Dionex ACES 300, recycle
Eluent Source:	Dionex EGC-KOH capillary cartridge		B: QD Charge Detection, *normalized to chloride peak
Gradient:	1 mM KOH (5 min), 1–15 mM KOH (5–15 min), 15–30 mM KOH (15–23 min), 30–60 mM KOH (23–31 min), 60 mM KOH (31–45 min)	Sample Prep.:	Diluted 5-fold, filtered, 0.2 $\mu$ m
Flow Rate:	0.015 mL/min	Peaks:	1. Quinate 2. Lactate 3. Acetate 4. Glycolate 5. Propionate 6. Formate 7. Chloride 8. Malate- 9. Succinate 10. Oxalate 11. Phosphate 12. Citrate 13. Isocitrate
Inj. Volume:	0.4 $\mu$ L		
Column Temp.:	30 °C		
System Press.:	3600 psi		

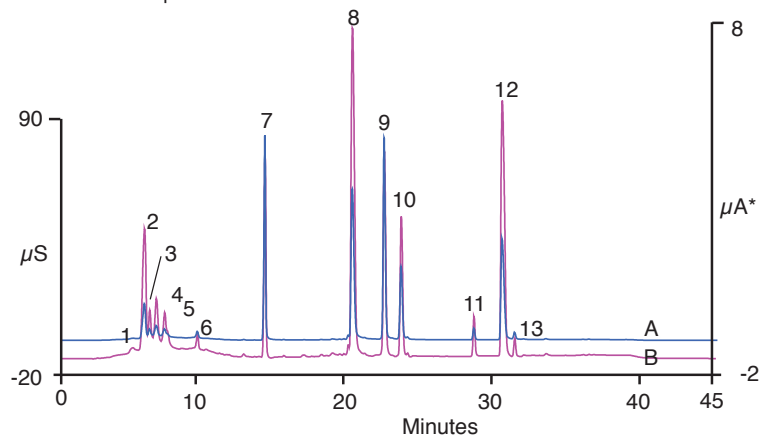


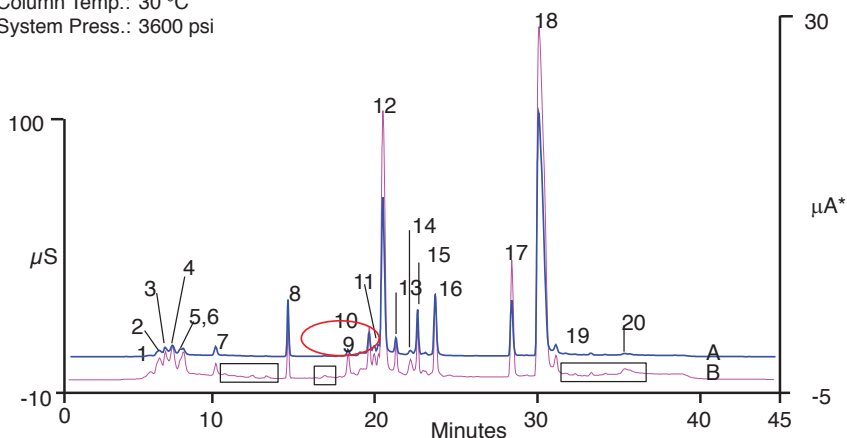
Figure 8 shows the QD chromatogram normalized at the chloride peak and overlaid on the CD chromatogram of a orange juice sample.<sup>2</sup> The chromatograms show a higher proportional charge with QD than CD for organic acids. Small organic acid peaks are detected in QD but not by CD (in square) and Peak 9 shows a higher QD response than expected suggesting the peak is not nitrate but an organic acid.

**FIGURE 8. Comparing CD to QD in a diluted orange juice sample to identify co-elution and detect additional peaks.**

Column: Dionex IonPac AS11-HC-4 $\mu$ m set, 0.4 mm  
 Eluent Source: Dionex EGC-KOH capillary cartridge  
 Gradient: 1 mM KOH (5 min), 1–15 mM KOH (5–15 min), 15–30 mM KOH (14–23 min), 30–60 mM KOH (23–31 min), 60 mM KOH (31–45 min)  
 Flow Rate: 0.015 mL/min  
 Inj. Volume: 0.4  $\mu$ L  
 Column Temp.: 30  $^{\circ}$ C  
 System Press.: 3600 psi

Detection: A: Suppressed conductivity, Dionex ACES 300, recycle mode  
 B: QD Charge Detection, \*normalized to chloride peak

Sample Prep.: Diluted 10-fold, filtered, 0.2  $\mu$ m



Peaks:	Peaks:	Peaks:	Peaks:
1. Quinate	6. Pyruvate	11. Unknown	16. Oxalate
2. Glycolate	7. Galacturonate	12. Malate	17. Phosphate
3. Lactate	8. Chloride	13. Maleate	18. Citrate
4. Acetate	9. Nitrate ?	14. Unknown	19. Isocitrate
5. Formate	10. Glutarate	15. Sulfate	20. Unknown

## Conclusion

The Dionex QD Charge Detector offered on the Dionex ICS-4000 HPIC system improves sample analysis and reporting reliability by:

- Detecting peaks previously not detected by CD.
- Identifying doubly and triply charged ions from the proportionally higher response than the singly charged ions.
- Providing more linear response and proportionally higher responses for weakly ionized than strongly ionized compounds by CD
- Detecting co-eluting peaks by the proportionally higher responses of multi-charged ions than singly charged ions.

## References

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