

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 QD Charge detection for Ion Chromatography (IC).

Methods: Inorganic anions and organic acids were separated on a high-capacity 4- μm particle Thermo Scientific™ Dionex™ IonPac™ AS11-HC-4 μm 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 μm 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). CD/QD ratios 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

Sample Preparation

Commercial juice samples were diluted and filtered (0.2 μm) with a syringe filter.

Ion Chromatography Instrumentation (Figure 1)

- Thermo Scientific™ Dionex™ ICS-4000 HPIC™ dedicated capillary IC system with
- Dionex IonPac ATC-500 trap column
- Thermo Scientific Dionex Conductivity Detection (CD) detector
- Dionex QD Charge Detector Cell (QDC)
- Thermo Scientific Dionex AS-AP Autosampler

TABLE 1. IC Conditions for Beverage Analysis.

| | |
|----------------|---|
| Column set: | Dionex IonPac AS11-HC-4 μ 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 μ L |
| Column Temp.: | 30 °C |
| Detection: | A: Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle mode, Thermo Scientific Dionex Carbonate Removal Device (CRD 180). B: QD Charge Detection, Dionex QDC cell, 6 V, recycle mode. |

FIGURE 1. Dionex ICS-4000 HPIC Dedicated Capillary System (FIGURE 1A), Interior view (FIGURE 1B), Thermo Scientific™ Dionex™ IC Cube™ with CD and QD Detectors (FIGURE 1C), QDC Charge Detector Cell (FIGURE 1D).

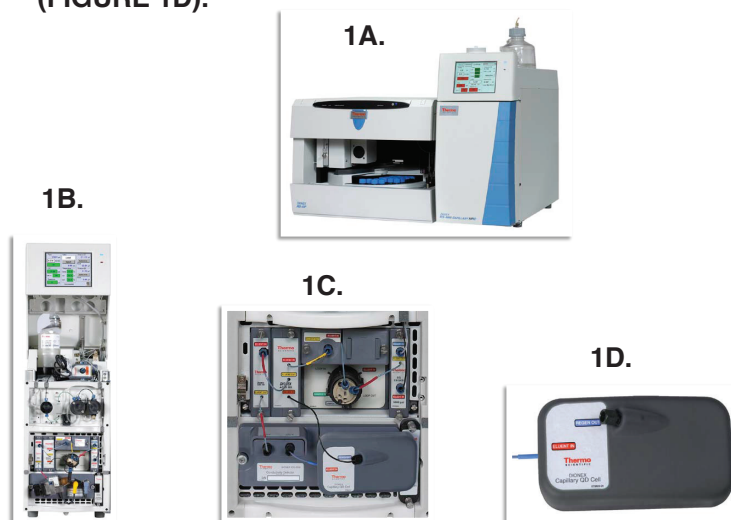
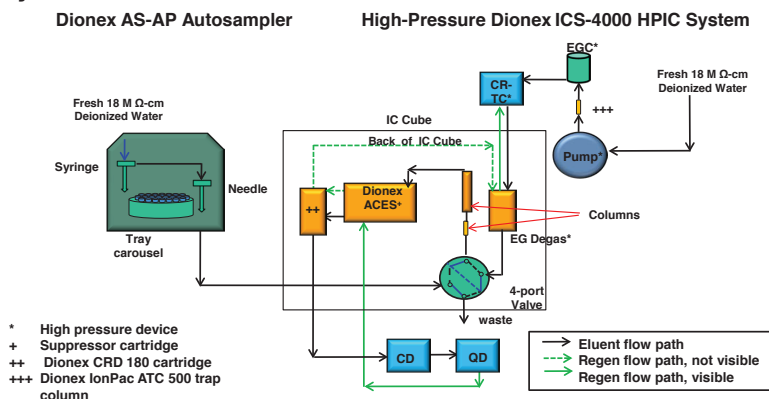


FIGURE 2. Flow Diagram of the Dionex ICS-4000 HPIC System



Data Analysis

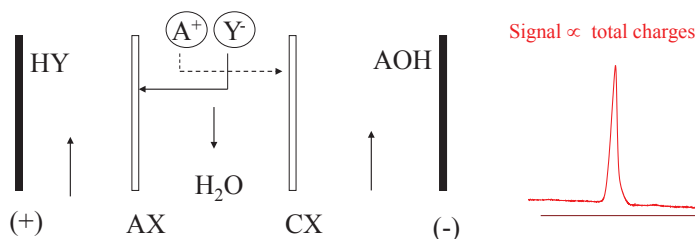
Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software

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).¹ 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.



Charge detection can be used to estimate concentration.¹ In charge detection, all the salts and acids with the same equivalency have similar responses (Figure 4) as compared with conductance where the salts have lower response.

FIGURE 4. Conductance versus Charge Detection.

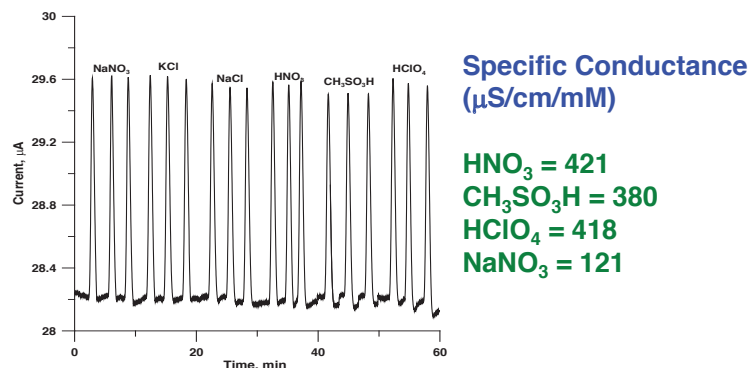


Figure 5 shows increased linear response for weakly ionized analytes with charge detection.¹

FIGURE 5. Compares CD (A) and QD (B) responses with concentration.

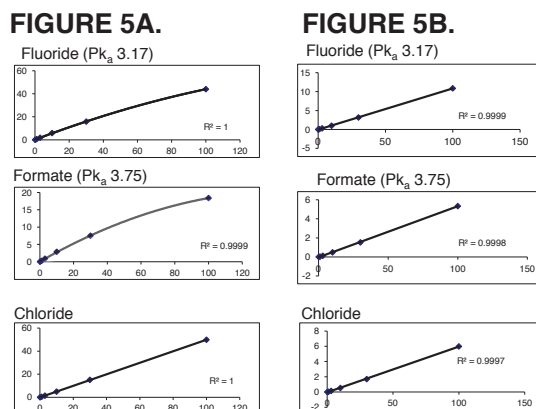


Figure 6 shows the QD chromatogram normalized at the chloride peak and overlaid on the CD chromatogram of a diluted guava juice sample.² The chromatograms show a higher proportional charge with QD than CD for organic acids in diluted guava juice.

FIGURE 6. Comparison of QD to CD Responses in Diluted Guava Juice

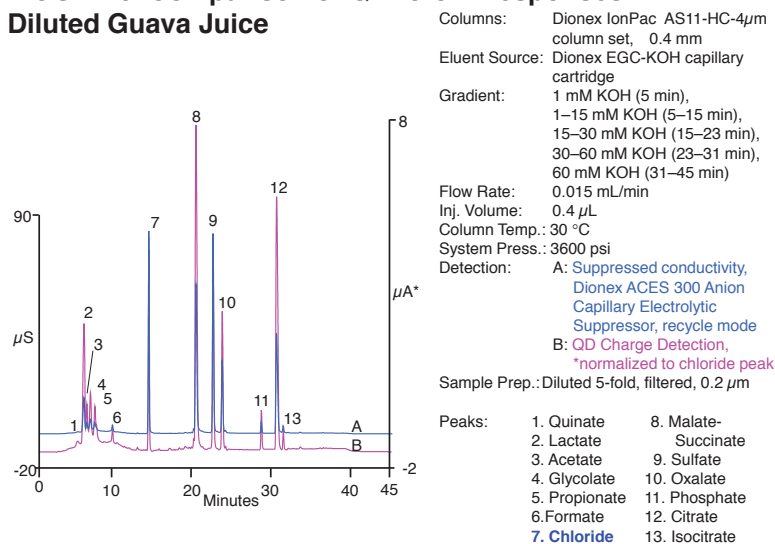


Figure 7 shows the higher proportional response of charge detection compared to conductivity detection for singly and multiply charged organic acids in a wine sample.³

FIGURE 7. Wine Sample, CD versus QD Response

Column: Dionex IonPac AG11-HC-4 μ m, Inj. Volume: 0.4 μ L
 Dionex IonPac AS11-HC-4 μ m, Temperature: 30 °C
 0.4 mm System Press.: 3600 psi
 Gradient: 1 mM KOH for 8 min, Detection: A) Suppressed conductivity,
 1–15 mM KOH (8 to 18 min); Dionex ACES 300,
 15–30 mM KOH (18 to 28 min); AutoSuppression, recycle mode
 30 to 60 mM KOH (28 to 38 min) B) Charge detection, 6 V, recycle
 mode
 Eluent Source: Dionex EGC-KOH (Capillary)
 Flow Rate: 0.015 mL/min

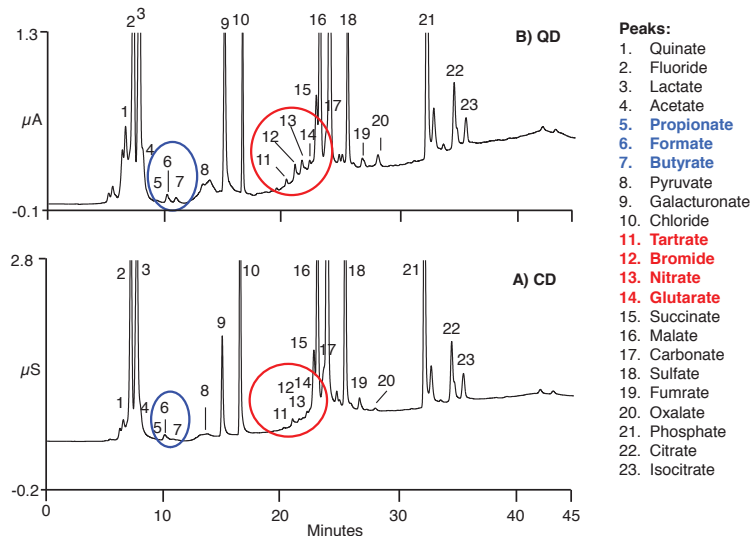
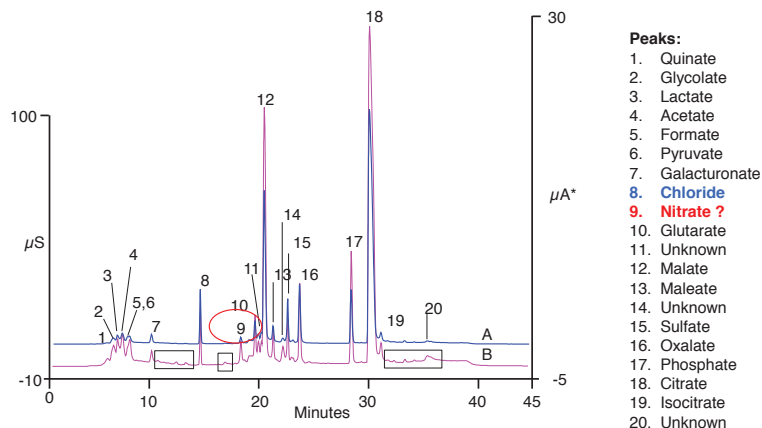


Figure 8 shows peaks in a diluted orange juice sample detected by QD but not CD (boxes).² Peak 9 is an example of using CD/QD for peak purity analysis. Peak 9 was initially identified as nitrate but exhibits the QD response of a doubly charged organic acid.

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 μ m set, Inj. Volume: 0.4 μ L
 0.4 mm Column Temp.: 30 °C
 Eluent Source: Dionex EGC-KOH (Capillary) System Press.: 3600 psi
 Gradient: 1 mM KOH (5 min), Detection: A) Suppressed conductivity,
 1–15 mM KOH (5–15 min), Dionex ACES 300 Anion Capillary
 15–30 mM KOH (14–23 min), Electrolytic Suppressor, recycle
 30–60 mM KOH (23–31 min), mode
 60 mM KOH (31–45 min) B) QD Charge Detection,
 *normalized to chloride peak
 Flow Rate: 0.015 mL/min
 Sample Prep.: Diluted 10-fold, filtered, 0.2 μ m



Conclusion

The 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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