

Determination of Inorganic Anions and Organic Acids in Beverages Using a Capillary IC on a Monolith Anion-Exchange Column

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Overview

Purpose: This method is used to determine inorganic anions and organic acids important to the beverage industry using capillary ion chromatography (IC). Organic acids are characteristic of the original fruit or plant. Profiling the organic acids in a beverage determines illegal adulteration of a costly fruit beverage by a less costly one.

Methods: Inorganic anions and organic acids in complex samples, such as beverage samples, were separated on a monolith-based capillary column optimized with anion-exchange chemistry to separate organic acids. The analytes were detected by suppressed conductivity after eluting from the column.

Results: This work demonstrates the advantages of using a capillary IC system that is always on and ready for analysis on demand. The results illustrate organic acid profiles of various juices and beverages, and the resolution and sensitivity possible with capillary IC using a capillary monolith column. Here, organic acid profiling is used to determine adulteration in beverage samples.

Introduction

In the multimillion dollar beverage industry, inorganic anions and organic acid determinations are important to characterize the beverage flavor, detect spoilage (indicated by acetic and formic acids), and determine adulteration by a less-costly juice illegally added to increase profits. Additionally, juice type and content and inorganic anion determinations are needed for beverage labeling requirements by regulatory agencies. These labeling requirements are used to identify adulterated beverages.

Capillary Reagent-Free™ ion chromatography (RFIC™) systems—the latest advancement in ion chromatography instrumentation—have multiple advantages as a result of miniaturizing IC from a 4 mm to a 0.4 mm platform:

- Less calibration
- No startup or equilibration time
- High $\mu\text{L}/\text{min}$ flow rates
- No eluent preparation

In this study, determinations of inorganic anions and organic acids in beverage samples demonstrate the sensitivity of the capillary IC system and the advantages of the Thermo Scientific Dionex IonSwift™ MAX-100 anion-exchange column, including:

- High efficiency
- Heightened resolution capabilities
- Faster flow rates

Methods

Sample Preparation

Beverage samples of brewed coffee and apple and orange juices were diluted 1:50 or 1:40, respectively as needed, filtered with the Thermo Scientific Dionex OnGuard™ RP cartridge, and 0.45 µm IC filtered prior to analysis.

Ion Chromatography Equipment and Data Analysis

Thermo Scientific Dionex ICS-5000 RFIC-Eluent Generation Capillary IC system (Figure 1) with:

- Thermo Scientific Dionex IC Cube™ capillary module (Figure 2)
- Thermo Scientific Dionex Chromeleon™ Chromatography Data System

Conditions

The conditions are described in the figures.

FIGURE 1. Dionex ICS-5000 Capillary IC system.

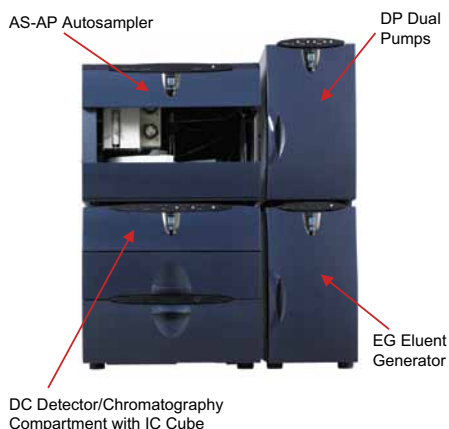
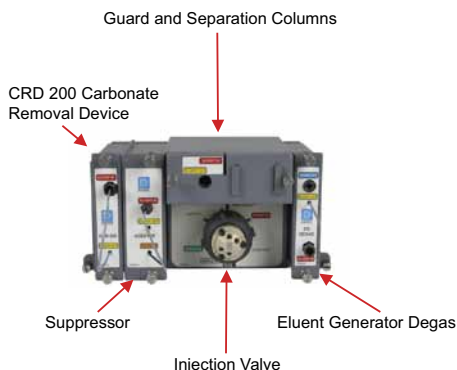


FIGURE 2. Dionex ICS-5000 IC Cube.

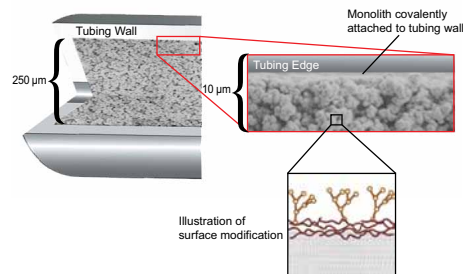


The capillary Dionex IonSwift MAX-100 column was selected for its high resolution, low column backpressure, speed, and selectivity for organic acid separations.

Dionex IonSwift Monolith Column

The Dionex IonSwift MAX-100 anion-exchange capillary column is a new separation media on a monolith backbone, created by in situ polymerization into a single-cylinder polymer rod which contains a continuous network of pores (Figure 3). The surface of the monolith backbone is modified with anion-exchange functional groups to have the selectivity of the Thermo Scientific Dionex IonPac™ AS11 hydroxide-selective anion-exchange column chemistry, optimized for organic acid separations and combined with the higher flow rate advantages of monolith columns.

FIGURE 3. Schematic of Dionex IonSwift MAX-100 monolith structure.



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Results

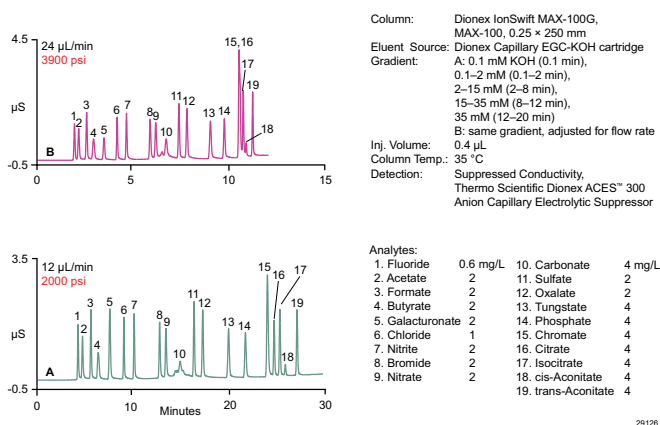
Advantages of Capillary IC

Scaling down the column size from analytical to capillary brings many advantages to ion chromatography. Capillary IC provides increased mass sensitivity, which means a smaller sample volume (0.4 µL) is needed to produce the same response as a standard bore system. Lower flow rates allow the IC system to be always on and ready for analysis on demand. Lower flow rates reduce eluent consumption (15 mL/day) and waste production, resulting in lower operating costs.

Speed Plus Resolution

Until recently, Reagent-Free IC system backpressures were maintained below 3000 psi to prevent damage to some of the devices. With the introduction of high-pressure capillary IC, the system is now capable of continuous operation up to 5000 psi. To reduce run times, the flow rate can be increased on the Dionex IonSwift MAX-100 column without losing resolution. Figure 4 shows chromatograms of 19 anions relevant to the beverage industry at flow rates from 12 and 24 $\mu\text{L}/\text{min}$, equivalent to 1.2 and 2.4 mL/min on a 4 mm column set platform. The same separation on the Dionex IonPac AS11 resin column (same chemistry as the Dionex IonSwift MAX-100) is typically 5 min longer.

FIGURE 4. Separation of 19 anion standards at increasing flow rates.

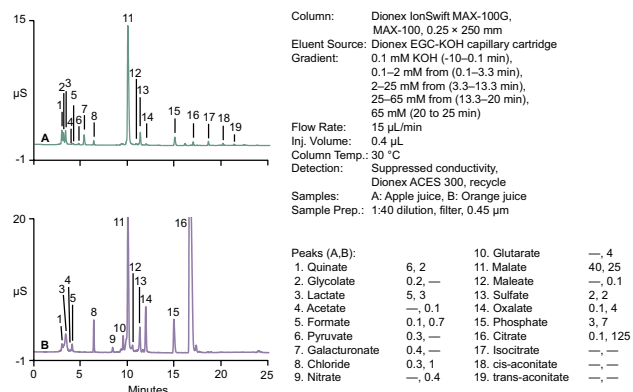


Analysis of Juice Samples

The method was applied to various beverage and juice samples (Figures 5–7). In Figure 5, the organic acid profiles of the lower cost apple juice and the higher cost orange juice are compared.

Typically, apple juice (Figure 5A) has low concentrations of citrate and other organic acids, whereas orange juice (Figure 5B) is more acidic and has much higher concentrations of citrate. These differences in profiles are used to determine illegally added apple juice in orange juice to increase profits.

FIGURE 5. Comparison of apple and orange juice organic acid profiles.



Analysis of Brewed Coffee Samples

The less costly Robusta varietal is commonly used in decaffeinated coffee and as an adulterant in the preferred and more costly Arabica varietal. Organic acid profiles of coffee are used to determine Robusta content in Arabica coffee. Additionally, organic acids are of interest because they are primarily responsible for the coffee's acidity. Figures 6 and 7 compare the differences in decaffeinated and caffeinated brewed coffee samples with the characteristic higher quinate (quinic acid) concentration present in the caffeinated coffee. Lower quinate and lower malate concentrations than normal would be indicative of adulteration by a Robusta varietal coffee.

FIGURE 6. Determination of anions and organic acids in a brewed decaffeinated coffee sample more typical of the lower cost Robusta coffee.

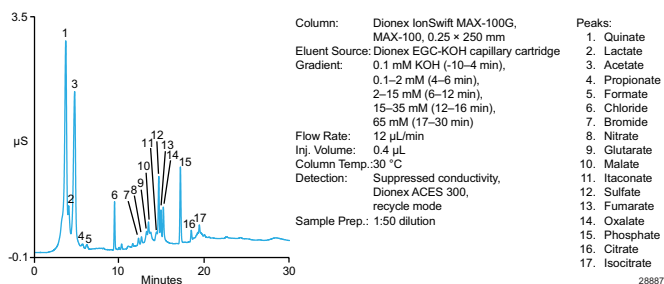
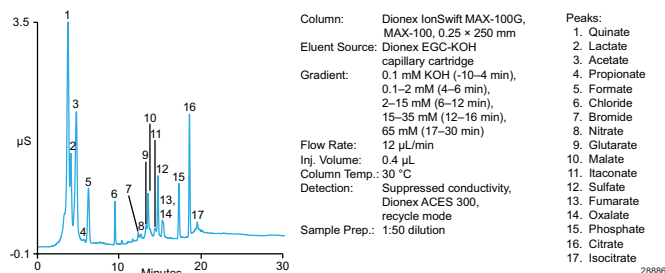


FIGURE 7. Determination of anions and organic acids in a brewed caffeinated coffee sample typical of the more costly Arabica coffee.



Conclusions

- Adulterations of beverages occur by illegally adding a similar, less costly product into a costly product for the purpose of increasing profits. This application demonstrates that profiling organic acids in beverages using capillary IC with the Dionex IonSwift MAX-100 column provides a valuable way to determine adulteration in complex samples.
- Profiling organic acids to report the percentage of juice types as mandated by the labeling requirements provides an effective method to determine adulteration.
- High-pressure capillary IC adds speed and sensitivity to the advantages of capillary IC, and complements the high-speed, high-resolution characteristics of the Dionex IonSwift MAX-100 anion-exchange capillary column to determine organic acids in complex samples, e.g., beverage samples.
- The high-pressure capillary IC system has all of the µL flow rate advantages of capillary IC, such as:
 - Adding only 1 L of water a month to generate eluent
 - Producing only 5 L of waste per year
 - Saving replacement costs of consumables

More information on beverage analysis and organic acid determinations can be found in Thermo Scientific Dionex Application Briefs and the Thermo Scientific Dionex Capillary IC Applications Library.^{1–3}

References

1. Thermo Fisher Scientific. Dionex Application Brief 135, Determination of Anions and Organic Acids in Brewed Coffee Samples Using Capillary IC. [Online] www.dionex.com/en-us/webdocs/110987-AB135-IC-AnionsOrganicAcids-Coffee-17Aug2011-LPN2916.pdf (accessed Sep 19, 2011).
2. Thermo Fisher Scientific. Dionex Capillary IC Applications Library, Food and Beverage Applications. [Online] www.dionex.com/en-us/documents/capillary-ic-library/food-beverage-capic/lp-110552.html (accessed Sep 19, 2011).
3. Thermo Fisher Scientific. Dionex Application Brief 135, Determination of Anions and Organic Acids in Apple and Orange Juices by Capillary IC. [Online] www.dionex.com/en-us/webdocs/110987-AB135-IC-AnionsOrganicAcids-Coffee-17Aug2011-LPN2916.pdf (accessed Sep 19, 2011).

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