Determination of Inorganic and Organic Acids in Apple and Orange Juice Samples Using Capillary IC

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Introduction

Determinations of organic acids in fruit juices are used by the beverage industry for flavor characterization, identification of spoilage, identification of adulteration by a less costly juice, and product labeling. The concentrations, types, and ratios of organic acids are largely responsible for the flavors, tartness, and acidity; therefore, these organic acid analyses are important for delivering a consistent and fresh juice product. Additionally, two common organic acids, acetate and lactate, are caused by biological activity and are, therefore, a good indicator of an old juice that may be too spoiled for consumption.

Because each fruit juice has a characteristic profile of organic acids, these profiles can be used to identify the juice product and identify adulteration by another juice. Profiling organic acids is used to identify cheaper apple juice illegally added to a costly orange juice claiming to be 100% orange juice.[1] Profiling is also used to meet the recent United States Food and Drug Administration (FDA) labeling requirements in 21 CFR Part 101 to identify percent juice, and percent of each juice in juice-containing beverages.[2] More recently, with the increased popularity of high antioxidant-containing juices, profiling is being applied to pomegranate, grape, cranberry, coconut, and bilberry juices.[3–8]

Organic acid determinations in beverages by ion-exclusion chromatography were demonstrated in 1997, and in 1989–2010 by anion-exchange chromatography using Thermo Scientific™ Dionex™ IonPac™ AS11 and AS11-HC columns designed for organic acid separations.[5–7] More recently, the Thermo Scientific Dionex ICS-5000 capillary HPIC™ system and ion-exchange columns designed for capillary flow rates were introduced, including the Thermo Scientific Dionex IonSwift™ monolith columns. These monolith columns are a new generation of separation media, combining the monolith backbone and ion-exchange media for fast high-resolution separations of small molecules including organic acids and inorganic anions.

Capillary IC has the advantages of µL/min flow rates and low eluent consumption, which allows a continuously running and available IC system without additional consumable replacement costs. The capillary IC system is designed to run continuously, saving time spent on equilibrating and recalibration typically needed after each start-up. Combined, the monolith and capillary IC technology provide organic acid determinations similar to the Dionex IonPac AS11 columns but with shorter run times and low eluent consumption.

In this study, inorganic anions and organic acids in diluted filtered apple and orange juice samples were determined on a Dionex IonSwift MAX-100 anion-exchange column using electrolytically generated hydroxide gradient from 0.1–65 mM KOH over 25 min at 15 µL/min (Figure 1). The analytes were detected by suppressed conductivity using the Thermo Scientific Dionex ACES™ 300 Anion Capillary Electrolytic Suppressor designed for capillary IC. All analyte peaks eluted within 25 min, demonstrating the column's speed. The analyte peaks were also extremely narrow and sharp, typical of separations using the Dionex IonSwift MAX-100 column.

Both chromatograms show the organic acid profiles expected for apple and orange juices. The juice samples results are similar to those shown in Dionex (now part of Thermo Scientific) Application Note (AN) 143 using a 4 mm Dionex IonPac AS11-HC column. The apple juice (Figure 1A) has predominately malic acid shown as malate, as previously reported in AN 143 (Figure 4). The orange juice sample (Figure 1B) contains mostly citrate (citric acid) and malate, similar to what was previously reported in AN 143 (Figure 3). However, in this application using the Dionex IonSwift MAX-100 capillary column, all peaks elute 15 min faster than shown in AN 143, with only 5 L/yr of water used for eluent generation. More information on organic acid separations can be found in the aforementioned application documents. Additional information on the monolith column and capillary IC can be found in the product manuals.[9,10]

Sample Preparation

Dilute samples 1:40 with deionized water and filter (0.45 µm) prior to analysis.

Conclusion

All Thermo Scientific Dionex IC systems and IC consumables were used in this application: the Dionex ICS-5000 Capillary HPIC system with a DP Dual Pump, EG Eluent Generator, and DC Detection Chromatography modules; Dionex AS-AP Autosampler; and Thermo Scientific Dionex Chromeleon™ Chromatography Data System. The Dionex ICS-5000 DC module included a capillary Dionex CD Conductivity Detector and a Thermo Scientific Dionex IC Cube™ module. All experimental conditions are listed in Figure 1.

Column:	Dionex IonSwift MAX-100 guard, Dionex MAX-100, capillary, 0.25 mm
Eluent Source:	Dionex EGC-KOH capillary cartridge
Gradient:	0.1 mM KOH from -10 to 0.1 min, 0.1–2 mM from 0.1 to 3.3 min, 2–25 mM from 3.3 to 13.3 min, 25–65 mM from 13.3 to 20 min, 65 mM from 20 to 25 min
Flow Rate:	15 µL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ACES 300 Anion Capillary Electrolytic Suppressor, recycle
Samples:	A: Apple juice, B: Orange juice
Sample Prep.:	1:40 dilution, filter, 0.45 µm

Peaks:	A	B
1. Quinate	6	2 mg/L
2. Glycolate	0.2	—
3. Lactate	5	3
4. Acetate	—	0.1
5. Formate	0.1	0.7
6. Pyruvate	0.3	—
7. Galacturonate	0.4	—
8. Chloride	0.3	1
9. Nitrate	—	0.4
10. Glutarate	—	4
11. Malate	40	25
12. Maleate	—	0.1
13. Sulfate	2	2
14. Oxalate	0.1	4
15. Phosphate	3	7
16. Citrate	0.1	125
17. Isocitrate	—	—
18. *cis*-Aconitate	—	—
19. *trans*-Aconitate	—	—

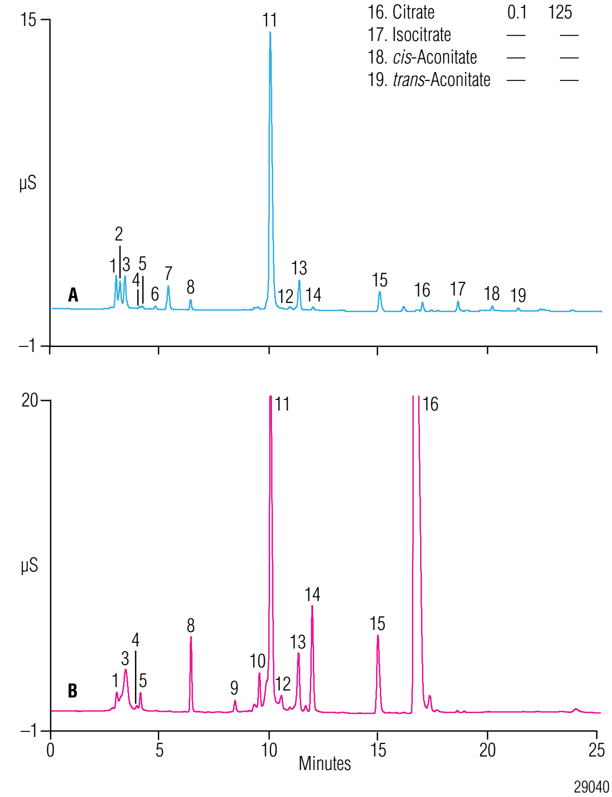

Figure 1. Inorganic anions and organic acids in diluted fruit juice samples.

References

1. Weiss, J. *Handbook of Ion Chromatography;* 3rd Ed.; VCH: Weinheim, Germany, 2000, pp 713–733.
2. Food Labeling. *Code of Federal Regulations,* Part 101, Title 21, *Fed. Regist.* **2010,** *2,* 76–78.
3. Thermo Fisher Scientific. *Anion Determinations of a Young Coconut Water Sample on a Dionex IonSwift MAX-100 Capillary Column.* Food and Beverage section in IC Capillary Library, Dionex (now part of Thermo Scientific) website, Sunnyvale, CA, 2011. http://www.dionex.com/en-us/images/pdf-cgram/cap-ic-applications/110969-28876-anion-organic-acid-coconut-water-IonSwift-MAX-100.pdf (accessed Sep 8, 2011).
4. Thermo Fisher Scientific. *Organic Acids in Wine.* Dionex (now part of Thermo Scientific) Application Note 21, LPN 03250, Sunnyvale, CA, 1989.
5. Thermo Fisher Scientific. *Determination of Inorganic Ions and Organic Acids in Non-Alcoholic Carbonated Beverages*. Dionex (now part of Thermo Scientific) Application Note 25, LPN 0662, Sunnyvale, CA, 1989.
6. Thermo Fisher Scientific. *Determination of Organic Acids in Fruit Juices.* Dionex (now part of Thermo Scientific) Application Note 143, LPN 1415, Sunnyvale, CA, 2003.
7. Thermo Fisher Scientific. *Determination of Organic Acids in Cranberry and Bilberry Extracts.* Dionex (now part of Thermo Scientific) Application Brief 112, LPN 2560, Sunnyvale, CA, 2010.
8. Thermo Fisher Scientific. *Higher Resolution Separation of Organic Acids and Common Inorganic Anions in Wine.* Dionex (now part of Thermo Scientific) Application Note 273, LPN 2727, Sunnyvale, CA, 2011.
9. Thermo Fisher Scientific. *Dionex ICS-5000 Ion Chromatography Operator's Manual.* Doc. No 065342, Sunnyvale, CA, 2011.
10. Thermo Fisher Scientific. *Product Manual for Dionex IonSwift Monolith Anion Concentrator (MAC).* Doc. No 065387, Sunnyvale, CA, 2010.

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