

# Determination of Anions and Organic Acids in Brewed Coffee Samples Using Capillary IC

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Brewed coffee, one of the most popular beverages worldwide, is prepared from fermented and roasted coffee plant seeds (beans), typically *Coffea arabica* (Arabica). *Coffea canefora*, variant *robusta* (Robusta), provides a less desirable flavor, is less costly, and therefore is often blended or adulterated in Arabica to create less expensive coffees or to increase profits. Although the coffee experience is often highly individualistic, the characteristic aroma, acidity, and flavor of a coffee are attributed to the inorganic anions, organic acids, chlorogenic acid, and monosaccharides content. Organic acids—such as malic, quinic, acetic, formic, and citric—provide much of the acidity associated with coffee.

The organic acid content and profile are characteristic of the coffee type, coffee fruit (cherry) maturity, and extent of roasting.<sup>1-3</sup> Quinate is present at high concentrations of 5–16% in beans from immature cherries, whereas malate concentrations are higher and quinate concentrations are lower in beans from mature cherries. Higher malate and quinate concentrations are characteristic of Arabica rather than Robusta coffee beans. Organic acids are volatile compounds and thus the concentrations are reduced during the roasting process. Therefore, organic acid determinations are needed to characterize the Arabica bean maturity and extent of roasting. Additionally, these organic acid determinations can profile Robusta and Arabica coffees to determine Robusta content due to blending or adulteration.

The capillary Reagent-Free™ ion chromatography (RFIC™) system is the latest advancement in IC instrumentation, with corresponding supporting columns, suppressors, and eluent generator cartridges. This miniaturization from standard bore and microbore technology to capillary (0.4 mm diameter) brings multiple advantages to IC:  $\mu\text{L}/\text{min}$  flow rates, low consumption of water (15 mL a day) and resulting low waste generation, and increased mass sensitivity.

In this study, inorganic anions and organic acid anions in caffeinated and decaffeinated brewed coffee samples are separated within 20 min by anion-exchange chromatography on a capillary Thermo Scientific™ Dionex™ IonSwift™ MAX-100 (0.25 × 250 mm) column set using a gradient of potassium hydroxide eluent at 12  $\mu\text{L}/\text{min}$ . The eluent is electrolytically generated in-line. The capillary monolith Dionex IonSwift MAX-100 anion-exchange column combines the higher flow rate advantages of monoliths with the Thermo Scientific Dionex IonPac™ AS11 chemistry optimized for organic acid separations. This results in 5 min shorter run times with the same resolution. The analytes are detected by suppressed conductivity detection as they elute from the column using the Thermo Scientific Dionex ACES™ Anion Capillary Electrolytic Suppressor specifically optimized for capillary IC. In this method, the Thermo Scientific Dionex ICS-5000 system is used at capillary flow rates to provide anion determinations needed to monitor coffee maturation, ensure coffee bean quality, and to determine extent of adulteration in purchased beans.

Figures 1 and 2 show the separation of 0.4  $\mu\text{L}$  injections of 1:50 diluted caffeinated and decaffeinated brewed coffee samples, respectively. The largest peaks in the caffeinated coffee sample (Figure 1) are the organic acid anions—quinate, formate, malate, and citrate—and the inorganic anions—chloride and phosphate. In the decaffeinated coffee sample (Figure 2), the quinate, lactate, and malate peaks are smaller than those found in the caffeinated coffee sample, and formate and citrate are nearly absent. The larger quinate and malate peaks in the caffeinated coffee sample, as compared to the decaffeinated coffee, agree with the literature, suggesting that the caffeinated and decaffeinated coffees are likely from Arabica and Robusta coffee beans, respectively.

Column: Dionex IonSwift MAX-100 guard,  
MAX-100 capillary,  
0.25 × 250 mm  
Eluent Source: Dionex EGC-KOH capillary  
Gradient: 0.1 mM KOH from -10 to 4 min,  
0.1–2 mM from 4 to 6 min,  
2–15 mM from 6 to 12 min,  
15–35 mM from 12 to 16 min,  
65 mM from 17 to 30 min  
Flow Rate: 12 µL/min  
Inj. Volume: 0.4 µL  
Column Temp.: 30 °C  
Detection: Suppressed conductivity,  
Dionex ACES Anion Capillary  
Electrolytic Suppressor,  
recycle mode  
Sample Prep.: 1:50 dilution

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Gradient: 0.1 mM KOH from -10 to 4 min,  
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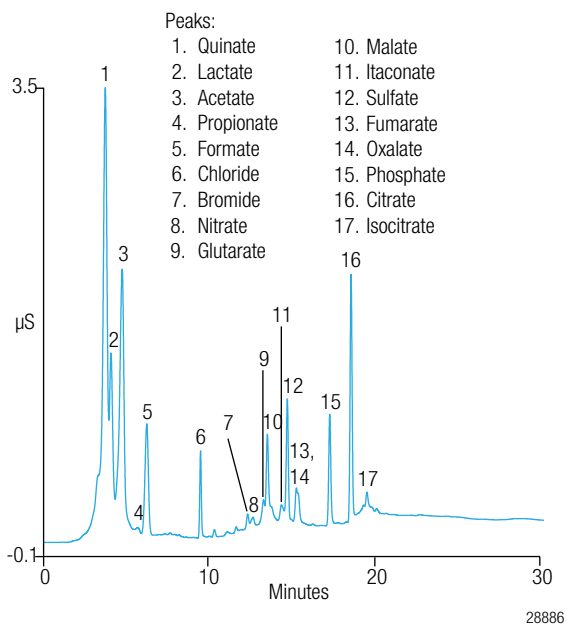


Figure 1. Separation of anions in a brewed caffeinated coffee sample by capillary IC on a Dionex IonSwift MAX-100 column.

## Conditions

A Dionex ICS-5000 capillary RFIC system with the Thermo Scientific Dionex IC Cube™ module, a Thermo Scientific Dionex AS-AP Autosampler, and Thermo Scientific Dionex Chromeleon™ Chromatography Data System software were used for all analyses. The chromatography conditions are listed in the figures. The injection valve was reset to Load position at 3 min in the gradient program to ensure good retention time precision of the early eluting organic acids.

## Sample Preparation

Brewed coffee from ground caffeinated and decaffeinated coffee bean samples was prepared using Sunnyvale, CA municipal water and then diluted 1:50 with deionized water prior to analysis.

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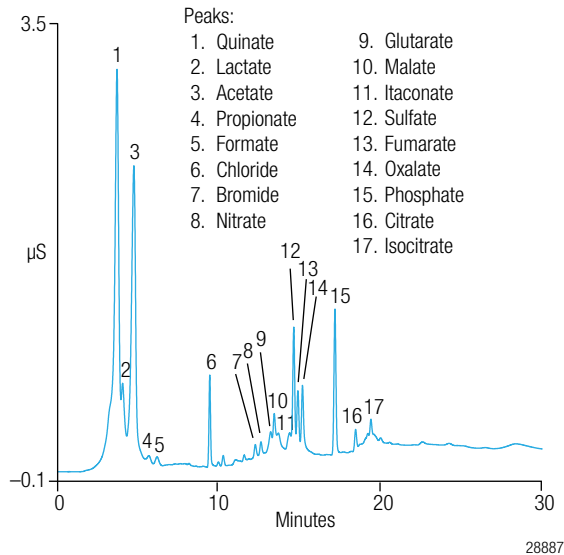


Figure 2. Separation of anions in a brewed decaffeinated coffee sample by capillary IC on a Dionex IonSwift MAX-100 column.

## References

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