Detection and Quantification of Inorganic Arsenic in Fruit Juices by Capillary Ion Chromatography with Suppressed Conductivity Detection

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Overview

Purpose: To demonstrate the detection and quantification of inorganic arsenic (arsenate As(V) and arsenite As(III)) in fruit juices using high-pressure capillary ion chromatography (IC) with suppressed conductivity detection (CD).

Methods: A 40-min gradient IC method was developed to separate 27 anions, including arsenate. This method was applied to the analysis of fruit juice samples.

Results: The gradient separation of 27 organic and inorganic acids was achieved on a high-capacity 4 µm resin particle ion-exchange column. Arsenate was well separated from citrate. The limit of detection (LOD) and limit of quantification (LOQ) for arsenate was 0.026 and 0.088 mg/L, respectively. Arsenite was converted to arsenate during this analysis. Therefore, the method detects and quantifies the total inorganic arsenic (arsenate As(V) and arsenite As(III)) in fruit juices.

Introduction

Growing interest around arsenic (As) determinations in fruit juices has been triggered by media claims of arsenic concentrations above acceptable limits in apple juice products. Total arsenic determinations can be misleading because inorganic forms of arsenic (arsenate As (V) and arsenite As(III)) are highly toxic while the organic forms have much lower toxicity.[1] IC is an established method to separate arsenic species. Combined with suppressed conductivity detection, this method provides a lower cost solution to characterize fruit juices and wine.[3,4] Recently introduced high-pressure capable capillary IC systems combined with 4-µm particle ion-exchange columns have reduced eluent consumption and improved separation efficiency. This study presents the detection and quantification of inorganic arsenic (arsenate As(V) and arsenite As(III)) in fruit juices on a 4 µm particle anion–exchange column using a high-pressure capillary IC system.

Methods

Sample Preparation

1000 mg/L stock standards were prepared by dissolving acids or salts in 18 MΩ-cm resistivity deionized (DI) water. Mixed working standards was prepared by mixing the stock standards and DI water.

Arsenate Calibration Standards was prepared by diluting the arsenate stock solution with DI water. 0.2, 0.5, 1.0, 4.0, 5.0, 10, 25, 50, and 100 mg/L arsenate standards were used.

Juice samples were commercial products filtered with a syringe filter (0.20 *μ*m), diluted 50-fold with DI water, spiked with 0, 0.19 and 0.50 mg/L arsenate.

Ion Chromatography Conditions

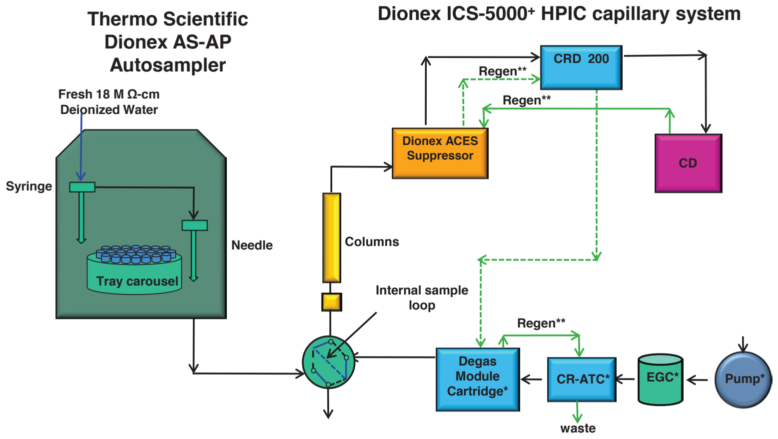
Instrument: Thermo Scientific™ Dionex™ ICS-5000$^+$ HPIC™ capillary system
Column: Thermo Scientific™ Dionex™ IonPac™ AS11-HC-4μm, 0.4 × 250 mm
Eluent Source: Thermo Scientific Dionex EGC-KOH capillary cartridge
Gradient: 1.5–2 mM KOH (0 to 2 min); 2–8 mM (2 to 13 min), 8–28 mM (13 to 25 min), 28–35 mM (25 to 33 min), 35–65 mM (33 to 34 min), 65 mM (34 to 38 min).
Flow Rate: 0.0150 mL/min
Inj. Volume: 0.40 μL
Column Temp.: 30 °C
IC Cube Temp.: 15 °C
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ AutoSuppression™ Device, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle mode

Data Analysis

Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software 7.1.

Figure 1 shows the chromatographic system flow diagram.

FIGURE 1. System Flow Diagram

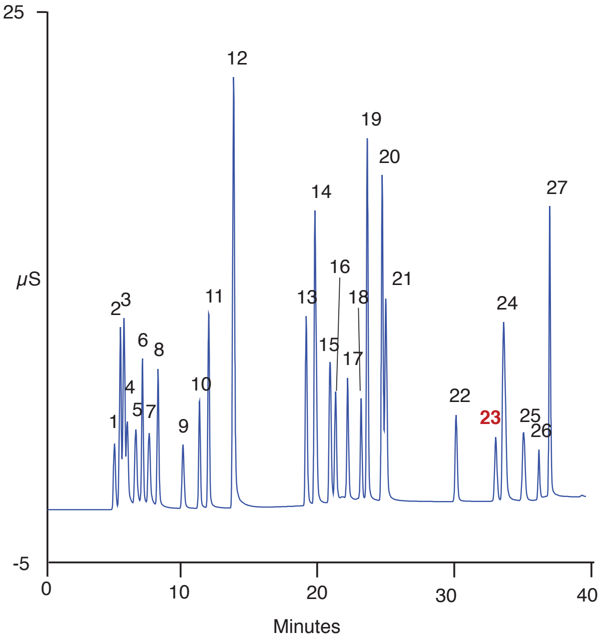


* High Pressure up to 5000 psi
** Green line is the flow path for Regen and dashed line shows flow through the back of the Thermo™ Scientific™ Dionex™ IC Cube

Results

Figure 2 shows the separation of 27 organic and inorganic acids in a single injection of the mixed standard for fruit juice analysis. Arsenate eluted at 32.9 min (Peak 23) and was well resolved from citrate.

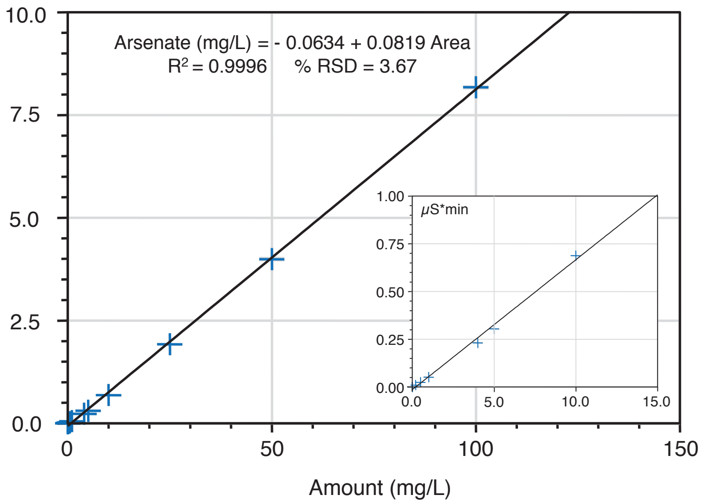
FIGURE 2. Mixed Standard for Fruit Juices Analysis.



Peaks:	mg/L
1.Quinate	9.3
2.Fluoride	2.3
3.Lactate	16.7
4.Acetate	11.4
5.Propionate	8.6
6.Formate	10.4
7.Butyrate	9.4
8.Pyruvate	10.8
9.Galacturonate	13.2
10.Bromate	7.8
11.Chloride	4.0
12.Nitrite	20.1
13.Bromide	10.1
14. Nitrate	11.5
15. Glutarate	13.1
16. Malate/Succinate	10.1
17. Malonate/Tartrate	9.6
18. Maleate	7.9
19. Sulfate	10.0
20. Oxalate	8.9
21. Fumarate	9.0
22. Phosphate	9.3
23. Arsenate	9.4
24. Citrate	25.4
25. Isocitrate	9.5
26. *cis*-Aconitate	11.4
27. *trans*-Aconitate	11.8

The calibration curve of arsenate was generated from 0.2 to 100 mg/L (Figure 3). Based on the signal to noise ratio (S/N), the arsenate LOD is 0.026 mg/L (S/N = 3, n = 5) and LOQ is 0.088 mg/L (S/N = 10, n = 5). Respectively, the LOD and LOQ for arsenic (As) is 0.014 and 0.047 mg/L,. These amounts are slightly higher than the EPA arsenic limit of 0.010 mg/L for drinking water and well above the reported Lowest Observed Adverse Effect Level (LOAEL) of 0.17 mg/L.[1]

FIGURE 3. Calibration Curve of Arsenate, 0.2–100 mg/L



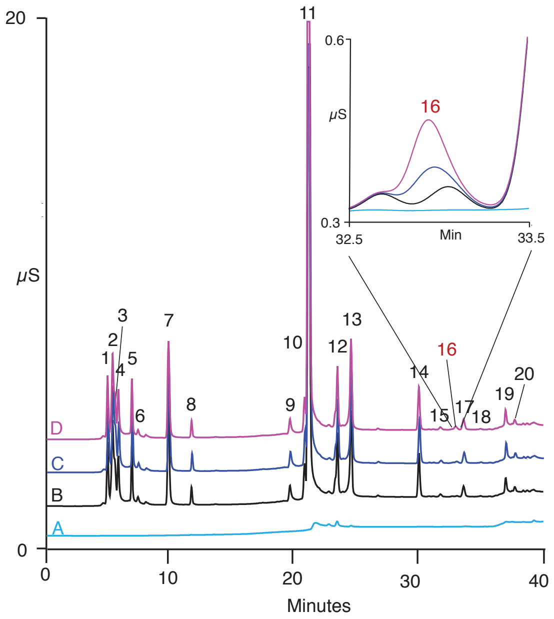
Arsenite was not detected with this method, however a corresponding concentration of arsenate was detected. Researchers reported that ~ 100% of As(III) was converted to the favored state, As(V), in tetramethylammonium hydroxide.[5] Freshly prepared arsenite samples under most pH conditions were run during this study. It was found that arsenite was converted to arsenate for all arsenite samples (data not shown). The eluent for this method, KOH, is also a strong base, which could convert arsenite to arsenate. Therefore, arsenate measurements likely include arsenite converted to arsenate and can be used to report approximate concentrations of total inorganic arsenic in the sample.

Analysis of Juice Samples

Six juice samples were studied: grape, mango, cranberry juice cocktail, and three brands of apple. Only apple juice samples had the peak associated with arsenate.

Figure 4 compares the results of a diluted apple juice sample with the same sample spiked with arsenate. The chromatograms also have the characteristics of an apple juice sample, very little citrate and predominantly malate.

FIGURE 4. Apple Juice Analysis.

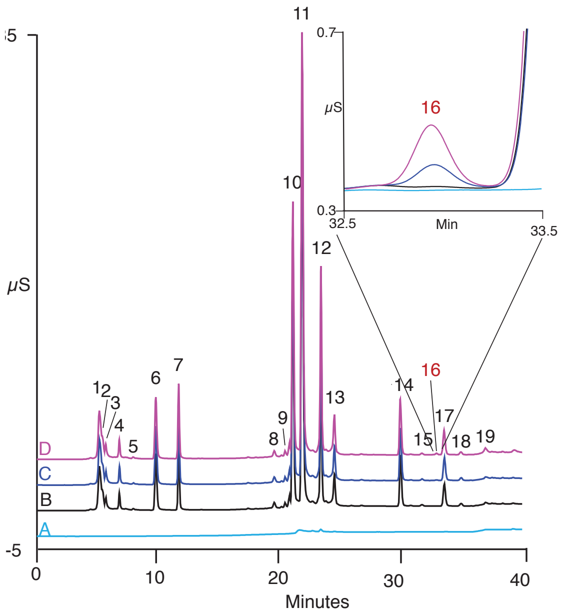


Peaks:	mg/L
1.Quinate	6.2
2.Fluoride	1.0
3.Lactate	2.1
4.Acetate/Glycolate	3.7
5. Formate	2.6
6. Pyruvate	0.4
7. Galacturonate	15.7
8. Chloride	0.3
9. Nitrate	1.1
10. Glutarate	0.3
11. Malate/Succinate	73.5
12. Sulfate	1.5
13. Oxalate	2.1
14. Phosphate	3.9
15. Unknown	-
16. Arsenate *	
17. Citrate	0.5
18. Isocitrate	0.2
19. *trans*-Aconitate	0.3
20. Unknown	-

Samples:
A: Water blank
B. 50-fold dilution of apple juice
C. Sample B + 0.19 mg/L arsenate
D. Sample B + 0.50 mg/L arsenate

Figure 5 shows the results of similar experiments with a diluted grape juice sample. The chromatograms have the expected characteristics of a grape juice sample, predominantly malate and Tartrate.

FIGURE 5. Grape Juice Analysis.



Peaks:	mg/L
1.Quinate	14.8
2. Lactate	2.1
3.Acetate/Glycolate	1.9
4. Formate	1.6
5. Pyruvate	0.4
6. Galacturonate	19.1
7. Chloride	2.4
8. Nitrate	1.0
9. Glutarate	na
10. Malate/Succinate	39.7
11. Malonate/Tartrate	63.6
12. Sulfate	7.8
13. Oxalate	1.5
14. Phosphate	9.2
15. Unknown	-
16. Arsenate *	
17. Citrate	3.9
18. Isocitrate	0.7
19. *trans*-Aconitate	-

Samples:
A: Water blank
B. 50-fold dilution of grape juice
C. Sample B + 0.19 mg/L arsenate
D. Sample B + 0.50 mg/L arsenate

Conclusion

- IC with suppressed conductivity detection provides a sensitive method to detect and quantify arsenite (As(III)) and arsenate (As(V)) as total inorganic arsenic, as well as characterizing organic acids.
- This method is sensitive with arsenate LODs and LOQs of 0.026 and 0.088 mg/L, respectively.
- Within the six juice samples were studied, only apple juice samples had the peak associated with arsenate.

A technical note including details of this study will be published in 2013.

References

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