

Ion Chromatography ICP-Q-MS for the Detection of Arsenic Species in Apple Juice

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Overview

Purpose: This paper describes and assesses the coupling of the Thermo Scientific Dionex ICS-5000 RFIC system to the Thermo Scientific XSERIES 2 ICP-Q-MS for the determination of inorganic and organic arsenic species in apple juice.

Methods: Anion-exchange chromatography coupled to the XSERIES 2™ ICP-Q-MS was used. The Thermo Scientific Dionex IonPac AS-7 column used in this study can separate both cationic and anionic species.¹

Results: A robust IC-ICP-MS system comprising a Dionex ICS-5000 system and an XSERIES 2 ICP-Q-MS was developed and shown to be a highly selective and sensitive technique for determination of trace element species.

Introduction

Interest in the determination of arsenic species in fruit juices has been triggered by recent media reports in the United States claiming that some apple juices may contain high amounts of arsenic (As).² Total arsenic was assessed in these reports however there was no investigation of the chemical form of the arsenic found. This is an important distinction because the inorganic forms of Arsenic (As³⁺ and As⁵⁺) are highly toxic, whereas the organic forms (e.g., arsenobetaine) are not considered toxic. Typical levels of total As found in apple juice are lower than the US EPA drinking maximum contaminant level (MCL) of 10 ng/g so apple juice is generally considered safe and is currently not regulated.³

Methods

Sample Preparation

Four different apple juices were purchased in a local supermarket. Aliquots of each sample were acidified and diluted, and the arsenic content determined using method of standard additions on the XSERIES 2 ICP-MS. One sample, in which no arsenic was found, was spiked with various amounts of arsenic species and analyzed to determine the spike recovery. The amount spiked was in the range of 10 to 20 ng/g, which meets or slightly exceeds the regulation set by US FDA for bottled water (10 ng/g). There is currently no regulation for arsenic levels in fruit juices. Samples which showed the presence of arsenic were then measured for arsenic species by IC-ICP-MS.

Liquid Chromatography

Chromatographic separations were carried out using the Dionex ICS-5000 ion chromatography system. Thermo Scientific Dionex anion-exchange columns supplied were used. Conditions can be found in Table 1.

TABLE 1. Conditions for chromatographic separations of As species	
Parameter	Value
Column	Dionex IonPac™ AS7 (2 mm i.d. 250 mm length)
Elution	Gradient elution (0.3 mL/min)
Mobile phase	A: 20 mmol/L Ammonium carbonate, pH 9 B: 200 mmol/L Ammonium carbonate, pH 9 Gradient from 20 to 200 mmol/L in 15 min
Injection volume	20 µL
Duration	15 min + column conditioning

ICP Mass Spectrometry

The XSERIES 2 ICP-Q-MS was used throughout this study. The operating parameters are summarized in Table 2. For the detection of arsenic, the collision cell was pressurized with helium to remove the spectral interference from ⁴⁰Ar³⁵Cl at m/z 75.

TABLE 2. Conditions for XSERIES 2 ICP-MS	
Parameter	Value
Forward power	1550 W
Nebulizer gas	0.80 L/min
Injector	2 mm i.d.
Cones	Xt
Cell gas flow / KED voltage	4.8 mL/min He/2V
Dwell time	100 ms

Figure 1. IC-ICP-MS system: Dionex ICS-5000 system coupled to XSERIES 2 ICP-Q-MS system



Results

Speciation of As in Apple Juice

A synthetic mixture containing 10 ng/g of six As species (inorganic As³⁺ and As⁵⁺, organic arsenobetaine [AsB], arsenocholine [AsC], monomethylarsonic acid [MMA], and dimethylarsinic acid [DMA]) was analyzed using the IC-ICP-MS system described above. Figure 2 shows the resulting chromatogram.

FIGURE 2. Chromatographic separation of six As species in dilute HNO₃

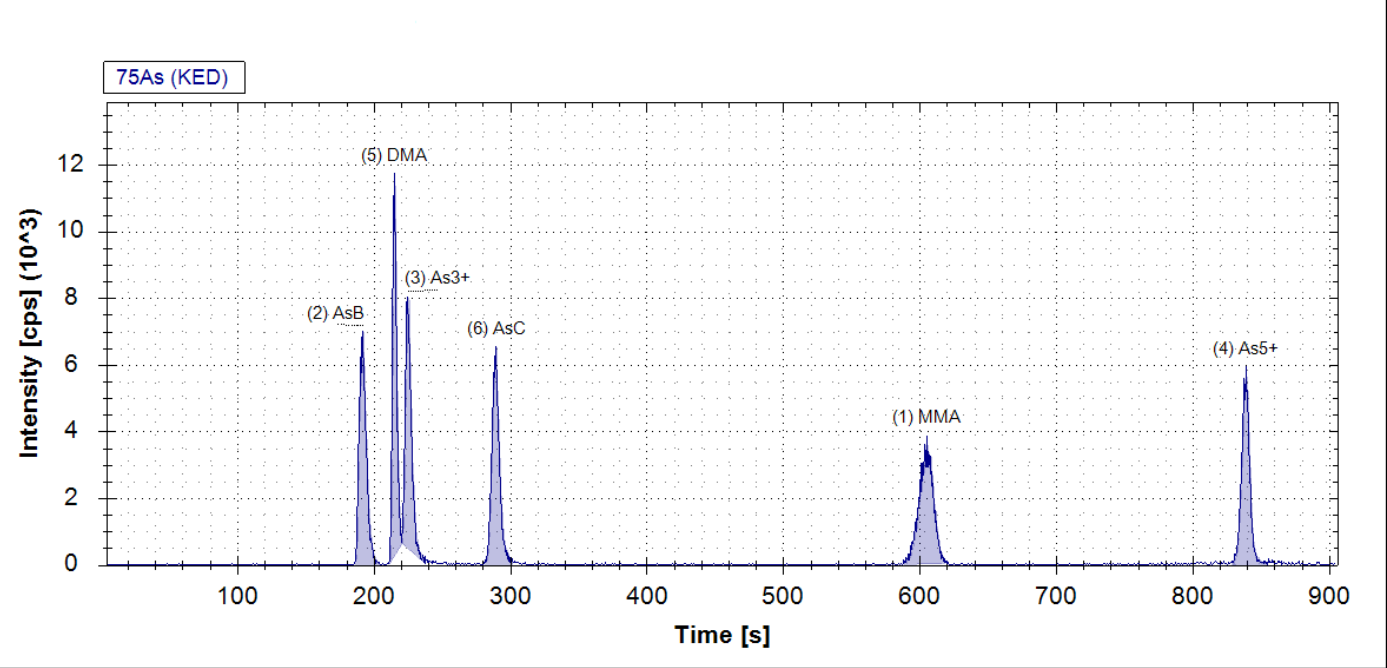
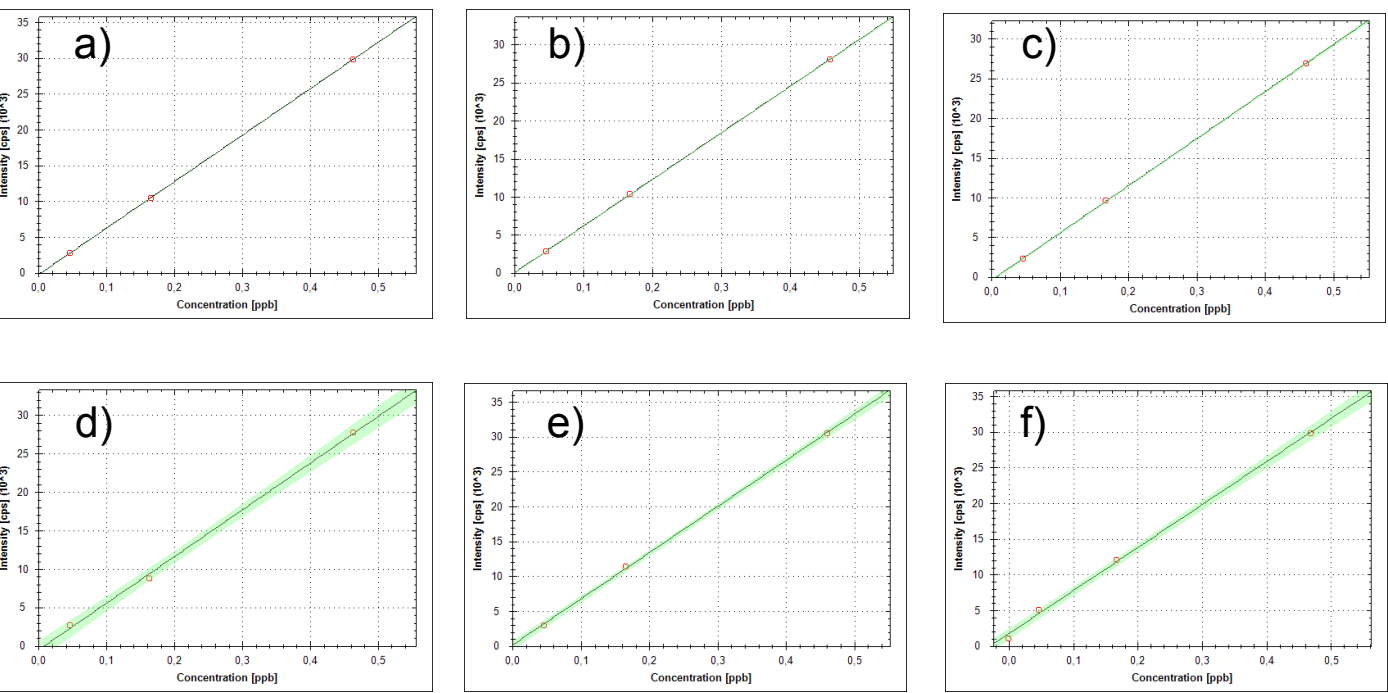


TABLE 3. Retention times and peak widths observed for the six As species measured		
Compound	Retention Time(s)	Peak Width(s)
AsB	185	15
DMA	205	10
As ³⁺	215	15
AsC	270	15
MMA	400	30
As ⁵⁺	800	20

The Thermo Scientific PlasmaLab software for the XSERIES 2 system features a complete chromatographic integration tool set which was utilized to integrate the individual peaks and determine the concentrations of each of the arsenic species. External calibration curves were prepared over a concentration range of 1 to 20 ng/g. The calibration curves for each of the six different arsenic species are shown in Figure 3, indicating excellent linearity and sensitivity.

FIGURE 3. Fully quantitative calibration graphs for AsB (a), DMA (b), As³⁺ (c), AsC (d), MMA (e), and As⁵⁺ (f).



Although DMA and As³⁺ elute at similar retention times (with a difference about 10 s, which leads to slight co-elution between both species), evaluation of the peak area was still possible with good accuracy using the chromatographic integration features of PlasmaLab software.

Detection limits were calculated based on three times the standard deviation of four repeat blank injections for each arsenic species. The detection limits are shown in Table 4 below.

TABLE 4. Detection limits for Arsenic species by IC-ICP-MS	
Compound	Detection Limit (pg/g)
AsB	2.3
DMA	3.8
As ³⁺	4.6
AsC	4.4
MMA	11.4
As ⁵⁺	1.2

Determination of Spike Recovery

Since initial analyses of locally sourced apple juices indicated no presence of As, a juice sample was spiked with varying amounts of the six As species under investigation and analyzed in order to determine the spike recovery.

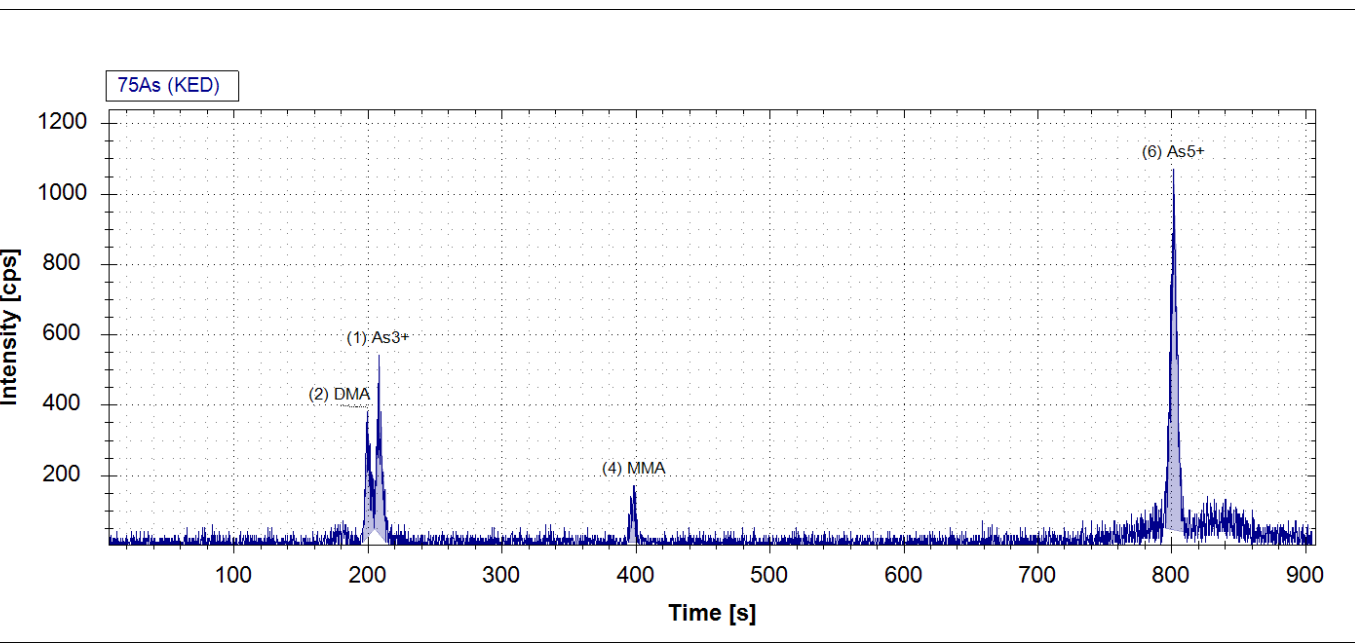
TABLE 5. Spike recovery obtained for six As species spiked into apple juice			
Species	Expected (ng/g)	Found (ng/g)	Recovery (%)
AsB	2.19	2.27	104
DMA	1.40	1.15	82
As ³⁺	1.35	1.38	102
AsC	1.94	1.87	94
MMA	1.09	1.13	104
As ⁵⁺	1.10	1.07	98

As can be seen from the results in Table 5, spike recovery was quantitative for all species except for DMA, which had a spike recovery in the range of 82%, possibly due to decomposition of the compound.

Speciation of Arsenic in Apple Juice Samples

Two juices in a subsequent batch were found to contain trace (~1.8 ng/g) levels of arsenic. These samples were then subjected to speciation analysis to determine whether the arsenic found was present in its nontoxic organic forms, or in its toxic inorganic species. The limit of detection (LOD) for the total As concentration was calculated to be 5 pg/g in the undiluted apple juice.

FIGURE 4. Chromatogram of an apple juice sample showing peaks for As³⁺ and As⁵⁺, MMA, and DMA



One of the resulting chromatographs is shown in Figure 4. The arsenic was identified as both the inorganic (toxic) species As³⁺ and As⁵⁺ and as the MMA and DMA organic forms. In the second juice sample, the arsenic was found only in the toxic inorganic forms.

The results of the species specific quantification are shown in Table 6 together with the total arsenic concentration determined previously. Each juice sample was analyzed in triplicate.

TABLE 6. Fully quantitative concentration of different As species and total As determined in apple juice samples					
Juice	DMA (ng/g)	As ³⁺ (ng/g)	MMA (ng/g)	As ⁵⁺ (ng/g)	Total As (ng/g)
Juice 3	-	0.5 ± 0.01	-	0.7 ± 0.01	1.7 ± 0.05
Juice 4	0.4 ± 0.05	0.3 ± 0.01	0.1 ± 0.05	0.7 ± 0.01	1.8 ± 0.05

The results for the arsenic speciation analysis and total arsenic analysis are in agreement. Other arsenic species being present in concentrations below the LOD might be responsible for the slight difference between the total As concentration and the sum of all species. The trace amounts of As found also correspond to the range of arsenic concentrations typically found in apple juices as published by the US FDA (between 2 and 6 ng/g).³

Conclusion

- The combination of the Dionex ICS-5000 ion chromatography system with the XSERIES 2 ICP-Q-MS provides a highly sensitive, routine IC-ICP-MS technique for the determination of trace metal species.
- A highly sensitive and specific method for the speciation analysis of arsenic in apple juice samples has been developed and applied to the analysis of different juices after a simple tenfold dilution.
- The Dionex IonPac AS7 anion-exchange column used in this study was not only able to efficiently separate six different arsenics species, but also helped to improve the sensitivity of the technique by concentrating each eluted species into a narrow peak. The low flow rate of 0.3 mL/min helps to reduce both sample and mobile phase consumption.

References

1. Dionex homepage <http://www.dionex.com/en-us/products/columns/ic-rfic/specialty-packed/ionpac-as7/lp-73274.html>
2. Letters from the FDA to the Dr. Oz Show Regarding Apple Juice and Arsenic <http://www.fda.gov/Food/ResourcesForYou/Consumers/ucm271746.htm>
3. Questions and Answers: Apple Juice and Arsenic: <http://news.consumerreports.org/Consumer%20Reports%20Arsenic%20Test%20Results%20January%202012.pdf>