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

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Overview

Purpose: Coupling of the Thermo Scientific Dionex ICS-5000 Ion Chromatography system to the new Thermo Scientific iCAP Q ICP-Q-MS is shown and assessed here for the determination of inorganic and organic As species in apple juice.

Methods: Anion exchange chromatography coupled to ICP-Q-MS was used. The Thermo Scientific Dionex IonPac AS-7 column used can separate both cationic and anionic species.[1]

Results: A routine coupling between the Dionex ICS-5000 and iCAP™ Q was achieved and shown to provide a highly sensitive speciation technique for the determination of trace element species.

Introduction

Increased interest in the speciation analysis of As in fruit juices has been triggered by recent media reports in the U.S. claiming that some apple juices may contain high amounts of As.[2] Only the total amount of As was assessed in these reports, without any investigation of the chemical form of As found—absolutely mandatory due to the high toxicity of the inorganic species As(III) and As(V) as opposed to the nontoxic organic species (e.g., arsenobetaine). However, as stated by FDA, typical levels of total As found in apple juice are low (below the drinking water limit of 10 ng g^{-1}) so apple juice is generally considered safe and is currently not regulated.[3]

Methods

Sample Preparation

Four different apple juices were bought in a local supermarket and the presence of As was determined after dilution in 7 mL of ultrapure water and 2 mL of 2% nitric acid using standard additions. One sample in which no As was found was spiked with different amounts of the sought As species and analyzed to determine the spike recovery. The amount spiked was in the range of 10–20 ng g^{-1}, which meets or slightly exceeds the FDA regulation for bottled water (10 ng g^{-1}), as there is currently no regulation for As levels in fruit juices. Samples which showed the presence of As were diluted likewise for speciation analysis.

Liquid Chromatography

Chromatographic separations were carried out using the Dionex ICS-5000 system with the Dionex IonPac™ AS-7 anion-exchange column. Complete conditions can be found below in Table 1.

TABLE 1. Conditions for chromatographic separations of As species.

Parameter	Value
Column	Dionex IonPac AS7 Analytical (2 × 250 mm)
Eluent	A: 20 mmol L^{-1} Ammoniumcarbonate, pH 9 B: 200 mmol L^{-1} Ammoniumcarbonate, pH 9
Gradient	20–200 mmol L^{-1} in 15 min
Flow rate	0.3 mL min^{-1}
Injection vol.	20 µL
Duration	15 min + column conditioning

ICP Mass Spectrometry

The iCAP Q ICP-Q-MS was used throughout this study. The operation parameters are summarized in Table 2. For the detection of As, the collision cell was pressurized with He in order to remove the spectral interference from $^{40}Ar^{35}Cl$ at m/z 75.

TABLE 2. Conditions for iCAP Q ICP-MS.

Parameter	Value
Forward Power	1550 W
Nebulizer Gas	0.80 L min^{-1}
Injector	2 mm i.D.
Cell Gas Flow/KED Voltage	4.8 mL min^{-1} He / 2V
Dwell Time	100 ms

FIGURE 1. iCAP Q ICP-MS and Dionex ICS-5000.

Results

Speciation of As in Apple Juice

In a model separation containing 10 ng g^{-1} of six As species, inorganic As(III) and As(V), organic arsenobetaine (AsB), arsenocholine (AsC), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) were separated. The resulting chromatograph is shown below in Figure 2.

FIGURE 2. Chromatographic separation of six As species in dilute HNO_3.

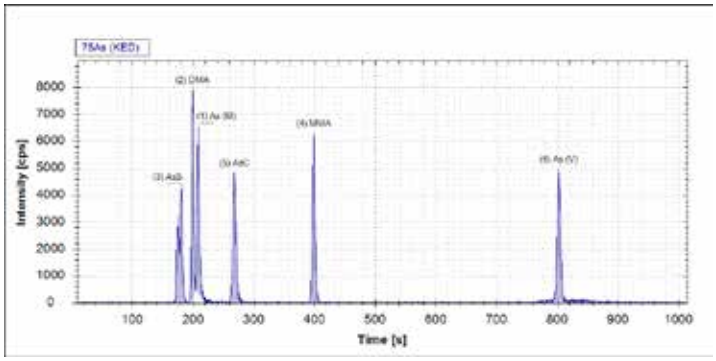
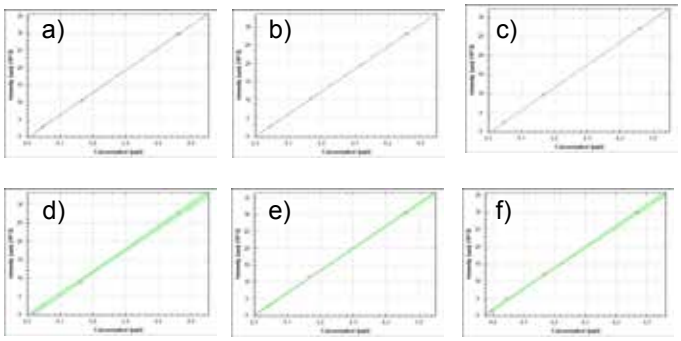


TABLE 3. Retention times and peak widths observed for the six As species measured.

Compound	Retention Times	Peak Widths
AsB	185	15
DMA	205	10
As(III)	215	15
AsC	270	15
MMA	400	30
As(V)	800	20

Evaluation of peak areas and concentrations was achieved in the iCAP Q ICP-Q-MS's Qtegra ICP-MS software. External calibration was used as a quantification strategy. In Figure 3, the calibration graphs obtained for the six different As species are shown, indicating good correlation and detection sensitivity.

FIGURE 3. Fully quantitative calibration graphs for a) AsB, b) DMA, c) As(III), d) AsC, e) MMA, and f) As(V).



Although DMA and As(III) elute at similar retention times (a difference of about 10s, leading to a slight coelution between both species), evaluation of the peak area was possible with good accuracy using the data acquisition features of the Qtegra ICP-MS software .

Limits of detection in undiluted juice from three * the standard deviation of four repeat blank injections were calculated to be 2.3 pg g^{-1} [AsB], 3.8 pg g^{-1} [DMA], 4.6 pg g^{-1} [As(III)], 4.4 pg g^{-1} [AsC], 11.4 pg g^{-1} [MMA], and 15.2 pg g^{-1} [As(V)].

Determination of Spike Recovery

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

TABLE 4. Spike recovery obtained for six As species spiked into apple juice.

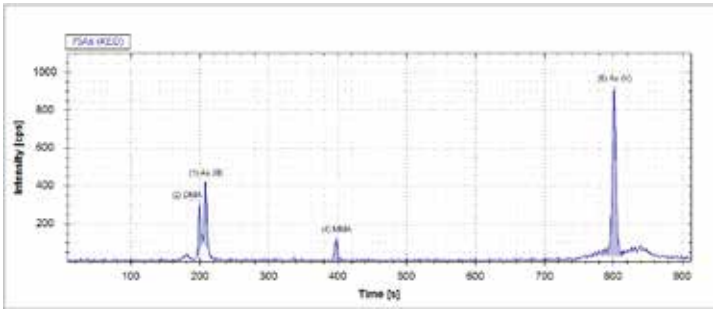
Species	Expected (ng g^{-1})	Found (ng g^{-1})	Recovery (%)
AsB	2.19	2.27	104
DMA	1.40	1.15	82
As(III)	1.35	1.38	102
AsC	1.94	1.87	94
MMA	1.09	1.13	104
As(V)	1.10	1.07	98

As can be seen from the results in Table 4, spike recovery was quantitative for all species except DMA, where spike recovery was only in the range of 82%.

Speciation of As in Apple Juice Samples

Two juices in a subsequent batch were found to contain trace (~1.8 ng g^{-1}) As levels. These samples were then subjected to speciation analysis to determine whether the As found was present in its nontoxic organic species, or in its toxic inorganic species. The limit of detection for the total As concentration was calculated to be 5 pg g^{-1} in the undiluted apple juice.

FIGURE 4. Chromatograph of an apple juice sample showing peaks for As(III) and As(V), as well as MMA and DMA.



One of the resulting chromatographs is shown in Figure 4. In this juice, As is found as the inorganic (toxic) species As(III) and As(V), but as well as in its organic species MMA and DMA. In the second juice, As was found only in the toxic inorganic species.

The results of the species specific quantification are shown in Table 4 together with the total As concentration determined previously. Each juice sample was analyzed in triplicate.

TABLE 5. Fully quantitative concentration of different As species and total As determined in apple juice samples.

Juice	DMA (ng g^{-1})	As(III) (ng g^{-1})	MMA (ng g^{-1})	As(V) (ng g^{-1})	Total As (ng g^{-1})
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

As can be seen from the above, the results of As speciation analysis and total analysis of As agree with each other. However, other As 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 determined amounts of As also correspond to the range of As concentrations typically found in apple juices as published by the FDA (between 2 and 6 ng g^{-1})[3].

Conclusion

- The combination of the Dionex ICS-5000 system with the iCAP Q ICP-Q-MS provides a highly sensitive, routine technique for the determination of trace metal species.
- A highly sensitive and specific method for the speciation analysis of As in apple juice samples has been developed and applied to the analysis of different juices after a simple ten-fold dilution.
- The Dionex IonPac AS7 column used was not only able to efficiently separate six different As species, but also helped to improve detection sensitivity as the separated species eluted with As narrow signals. The low flow rate of 0.3 mL min^{-1} helps to reduce both sample and mobile phase consumption.

References

1. Thermo Scientific Dionex IonPac AS7 Specialty Anion-Exchange Column. www.dionex.com/en-us/products/columns/ic-rfic/specialty-packed/ionpac-as7/lp-73274.html (accessed Jul 23, 2012).
2. U.S. FDA, Letters from the FDA to the Dr. Oz Show Regarding Apple Juice and Arsenic. www.fda.gov/Food/ResourcesForYou/Consumers/ucm271746.htm (accessed Jul 23, 2012).
3. Consumer Reports® Results of Our Apple Juice and Grape Juice Tests. http://news.consumerreports.org/Consumer%20Reports%20Arsenic%20Test%20Results%20January%202012.pdf (accessed Jul 23, 2012).

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