

# IC-ICP-MS speciation analysis of As in apple juice using the Thermo Scientific iCAP Q ICP-MS

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## Key Words

iCAP Q, Apple juice, As speciation, Ion chromatography, ICS-5000

## Goal

Apple juice samples are analyzed by IC-ICP-MS to determine the concentration of six arsenic species: two inorganic and toxic species (As (III) and As (V)) and four organic species (arsenobetaine (AsB), arsenocholine (AsC), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)).

## Introduction

Interest in the determination of arsenic (As) species in fruit juices has been triggered by media reports in the US claiming that some apple juices may contain high amounts of arsenic<sup>1</sup>. Since fruit juices are frequently consumed, especially by young children, the reported values have led to serious concerns about the safety of such products. However, in the experiments conducted, only the total arsenic concentration was assessed, but no detailed investigation of the chemical form of the element was carried out. This is an important distinction since the inorganic forms of arsenic (As (III) and As (V)) are highly toxic, while the organic forms (e. g. arsenobetaine) are not considered to be toxic. Typical levels of total arsenic 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<sup>2</sup>. However, as a consequence, the FDA is currently reviewing data, and may eventually tighten its current guidelines.

## Instrument configuration

Chromatographic separations were carried out using the Thermo Scientific Dionex ICS-5000 ion chromatography system. Due to its completely metal-free solvent pathway, this system is perfectly suited for elemental speciation studies. A Thermo Scientific Dionex AS-7 anion exchange column (2 mm ID x 250 mm length) was used throughout this study, as it is able to separate both cationic and anionic species<sup>3</sup> and is therefore well suited for the separation of the arsenic species under investigation. The Thermo Scientific iCAP Qc ICP-MS was used as highly sensitive and selective arsenic detector. Due to its unique, proprietary 90° ion optics (RAPID lens) the iCAP™ Qc provides both high elemental sensitivity and low backgrounds while high selectivity is achieved through the use of a He pressurized QCell in KED (Kinetic Energy Discrimination) mode that efficiently reduces polyatomic interferences in all sample types. Uniquely, the QCell He KED mode also includes a low mass filter that ensures the lowest background noise – particularly important for applications at low concentration levels. For the sensitive analysis of (monoisotopic) arsenic at m/z 75, there is no possibility to use a different isotope for analysis and therefore the flexible, non-matrix specific interference reduction QCell He KED mode was employed in order to minimize polyatomic interferences such as <sup>40</sup>Ar<sup>35</sup>Cl that would otherwise return a potentially serious false positive.

## General analytical conditions

The iCAP Qc ICP-MS was equipped with a Peltier cooled cyclonic PFA spray chamber and a PFA-LC nebuliser (Elemental Scientific, Omaha, NE, USA). The PFA-LC nebulizer has a very low dead volume and is compatible with LC fittings making it ideal for chromatographic analyses. A demountable torch was equipped with a 2 mm I.D. quartz injector. The instrument was optimized daily for optimum performance in He KED mode using the supplied autotune protocols.



The iCAP Qc ICP-MS was operated using the following parameters:

Parameter	Value
Forward power	1550 W
Nebulizer gas	0.80 L/min
Injector	2 mm I.D., quartz
Interface	Ni sampler and skimmer
QCell He gas flow	4.8 mL/min
QCell KED voltage	2 V
75As dwell time	100 ms

Table 1: iCAP Qc ICP-MS operating parameters.

Chromatographic separations were carried out on the ICS-5000 using the parameters summarized in Table 2. For the elution of the different arsenic species, anion exchange chromatography was chosen using a linear gradient from 20 to 200 mmol/L of ammonium carbonate. Under these conditions, complete elution of all detectable species was achieved in less than 15 minutes, making for a very high throughput, routine chromatographic analysis.

Column	Dionex AS-7 (2 mm I.D., 250 mm length)
Elution	Gradient
Mobile phase	A: 20 mmol/L Ammonium carbonate B: 200 mmol/L Ammonium carbonate Gradient from 20 to 200 mmol/L in 15 minutes
Injection volume	20 $\mu$ L
Duration	15 minutes

Table 2: ICS-5000 operating parameters.

The column outlet from the ICS-5000 was directly connected to the PFA-LC nebulizer. Full bi-directional communication between the instruments was achieved using a trigger cable connected to the I/O port on the right hand side of the iCAP Qc ICP-MS. All data evaluation was performed using the tQuant features of the Thermo Scientific Qtegra software.

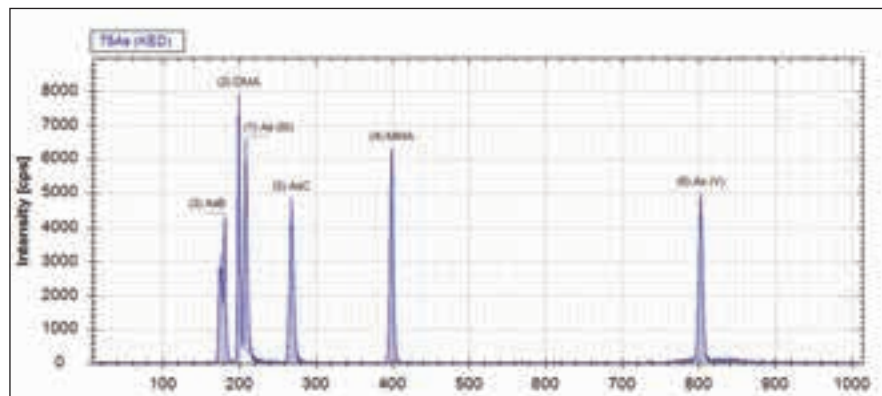


Figure 1: Model separation of six arsenic species, each at 0.45 ng/g in dilute HNO<sub>3</sub>.

## Sample and calibration solution preparation

Four different apple juices were bought in a local supermarket and the total arsenic concentration was first determined after dilution of 1 mL juice in 7 mL of ultrapure water / 2 mL of 2 % nitric acid. One sample, where no arsenic was found, was spiked with different amounts of the arsenic species investigated and analyzed to assess spike recovery in the juice matrix. The amount spiked was between 10 to 20 ng/g, meeting or slightly exceeding the regulation set by FDA for bottled water (10 ng/g). Samples that showed the detectable presence of total arsenic were passed for subsequent speciation analysis. All calibration standards and spiking solutions were prepared daily from stock solutions containing the different arsenic species at a concentration of 1 mg/L.

## Results and Discussion

The analysis of arsenic in food is a challenging task for analytical chemists. Total arsenic concentrations in food are usually very low since potential sources, such as arsenic containing pesticides, were phased out over 30 years ago. Additionally, ICP-MS detection of arsenic can be interfered by polyatomic species that limit its detection and might lead to falsely high results. The use of He KED as used in the iCAP Q ICP-MS however, has been shown to significantly reduce the impact of those polyatomic interferences in many sample types, for example <sup>35</sup>Ar<sup>40</sup>Cl in the case of <sup>75</sup>As. With the high transmission RAPID lens, sensitivities in He KED mode are more than sufficient for sub ng/g arsenic speciation analyses.

To show the detection power of He KED mode on the iCAP Qc ICP-MS, a model separation was performed from a sample of dilute HNO<sub>3</sub> containing 0.45 ng/g of six As species (As (III) and As (V) as toxic inorganic species, arsenobetaine (AsB), arsenocholine (AsC), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) as non toxic, organic As species).

As can be seen in Figure 1, all arsenic species are well resolved in less than 15 minutes. Precision of retention times are less than 4 %, and absolute peak widths were in the range of 10 - 20 s for all species. The reduced peak widths due to the advanced Dionex ion chromatographic

technology contribute significantly to the demonstrated sensitivity of the method and even low concentration species are easily detectable with such high signal-to-noise ratios. Although DMA and As (III) elute at similar retention times, accurate peak area determinations are still possible using the advanced peak detection and integration routines available in Qtegra™ software.

The fully quantitative calibration curves obtained for the six arsenic species measured are shown in Figure 2.

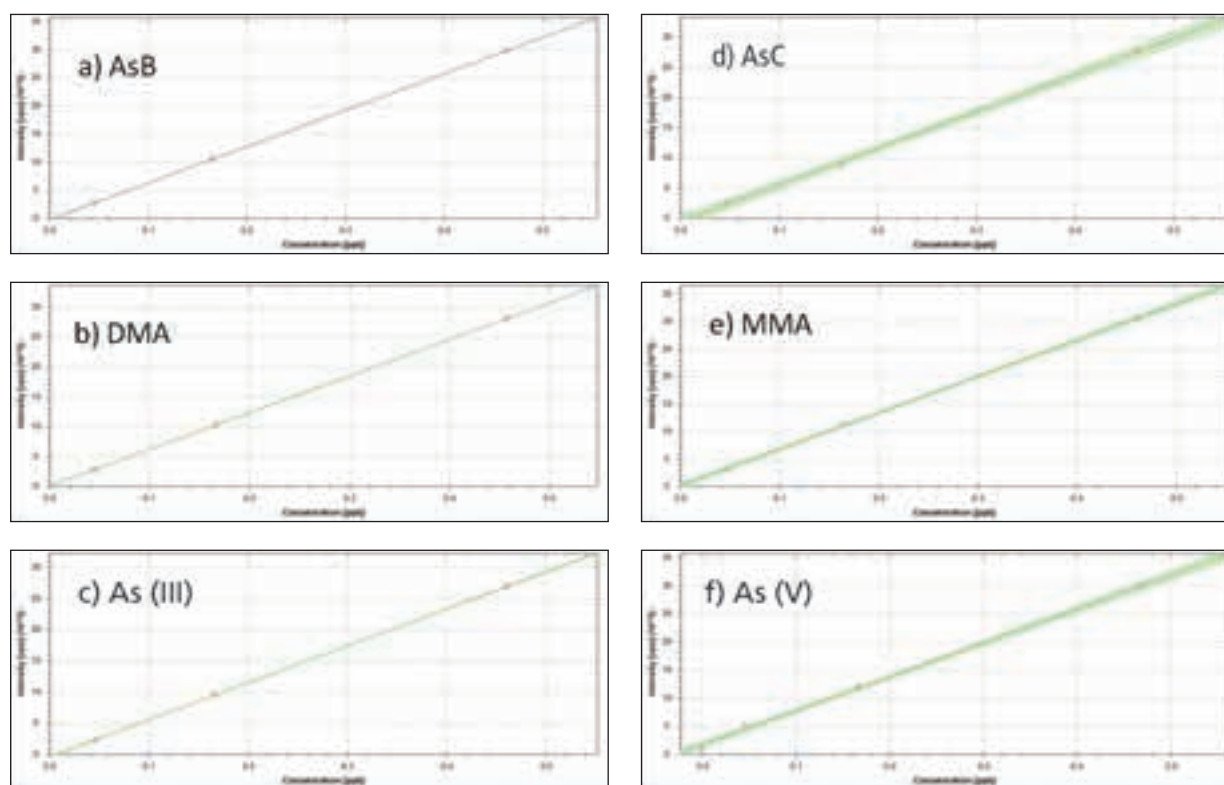


Figure 2: Fully quantitative IC-ICP-MS calibrations of six arsenic species with calibration points at 0.045, 0.165 and 0.45 ng/g.

Results from two of the four apple juices where arsenic was detected are summarized in Table 4. Method detection limits (MDLs) for the arsenic species were calculated from three times the standard deviation of four repeat blank injections. Total arsenic concentrations for the two samples are also shown.

	AsB	DMA	As <sup>3+</sup>	AsC	MMA	As <sup>5+</sup>	Sum of Total Species	As
MDL	0.002	0.004	0.005	0.004	0.011	0.001	-	0.005
Juice 3	ND	ND	0.5 ± 0.01	ND	ND	0.7 ± 0.01	1.2	1.7 ± 0.05
Juice 4	ND	0.4 ± 0.05	0.3 ± 0.01	ND	0.1 ± 0.05	0.7 ± 0.01	1.5	1.8 ± 0.05

Table 4: As species concentrations, method detection limits (MDLs) and total arsenic concentrations in two of the apple juice samples analyzed. All concentrations have units of ng/g. ND indicates not detected.

The sum of the arsenic species is slightly lower than the total arsenic concentration observed. Other arsenic species at concentrations below the LoD might be responsible for the slight difference between the total arsenic concentration and the sum of all species. Decomposition of the arsenic compounds before analysis may also have contributed to the observed difference. The trace amounts of arsenic found in this study fit well with a typical range of arsenic concentrations in apple juices (between 2 and 6 ng/g) as determined by the United States Food and Drug Agency (US FDA) in a previous study<sup>3</sup>.

In order to determine the robustness of the IC-ICP-MS method developed, an apple juice sample was spiked with varying amounts of the six arsenic species under investigation and analyzed by IC-ICP-MS. The amounts added to the juice were between 10 and 20 ng/g, which meets or slightly exceeds the regulation set by FDA for bottled water (10 ng/g). The juices were then diluted as before and analyzed using the IC-ICP-MS method developed. The resulting concentrations and calculated recoveries are shown in Table 5.

Species	Expected (ng/g)	Found (ng/g)	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

Table 5: Spike recovery for six arsenic species in apple juice.

As can be seen from the results in Table 5, spike recovery was quantitative for all species, with DMA being an exception, where spike recovery was only in the range of 82 % possibly due to possible decomposition of the compound.

## Conclusion

A new IC-ICP-MS method for the separation and quantification of six arsenic species in apple juice has been developed. The coupling of the ICS-5000 ion chromatographic system with the iCAP Q ICP-MS has been shown to be a powerful tool for the detection of low concentrations of arsenic species in fruit juices. The highly efficient separation achieved with the AS-7 anion exchange column combined with the high sensitivity of the iCAP Qc ICP-MS improves signal-to-noise ratios leading to significantly lower detection limits. The small dimensions of the AS-7 column allow for minimal sample consumption and reduced solvent volumes to reduce cost per analysis. The developed method offers high sample throughput that is crucial in food applications where large numbers of samples may have to be rapidly analyzed.

Although there is no legislative limit for arsenic species in fruit juices currently, the detection limits obtained by this method (~ 5 pg/g) far exceed those in similar sample types, e. g. bottled water (FDA limit set at 10 ng/g).

## References

1. Letters from the FDA to the Dr. Oz Show Regarding Apple Juice and Arsenic (<http://www.fda.gov/Food/ResourcesForYou/Consumers/ucm271746.htm>)
2. FDA arsenic in apple juice resources site: <http://www.fda.gov/Food/ResourcesForYou/Consumers/ucm271595.htm>
3. FDA arsenic in apple juice results: <http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm272705.htm>
4. Dionex homepage (<http://www.dionex.com/en-us/products/columns/ic-rfic/specialty-packed/ionpac-as7/lp-73274.html>)

## Chemicals Used in this Note

Chemical	Fisher Scientific Catalogue Number
IonPac AS7 Analytical Column (2 x 250 mm)	063097
Fisher Optima grade nitric acid	A467-500

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