Determination of Arsenic Species in Beverages by HPLC-ICP-MS

Challenge

Separation and quantification of arsenic species to identify harmless and toxic arsenic compounds.

Solution

A reliable and fast method for the separation of more than five As species by coupling a PQ LC HPLC system and a PlasmaQuant MS, ICP-MS.

Introduction

The species or chemical form of elements determines their mobility, bioavailability and toxicity. Liquid chromatography or ion chromatography allow a separation of these species. The subsequent detection by mass spectrometry provides a highly sensitive method for their quantification. Hence, LC-ICP-MS and IC-ICP-MS provide an essential tool for assessing benefits and/or risks of elements present in the sample.

An element can be essential and toxic just based on the oxidation state or compound in which it occurs. Thus, food samples like seafish, rice or chocolate, apple juice and other foods and beverages are controlled by LC-ICP-MS for arsenic, selenium or chromium species present.

Arsenic speciation plays an important role in the characterization of food samples since it is absorbed from the soil into food plants like rice or apple and orange trees. Mostly accumulated in the fruit, the related products need to be characterized for their arsenic content. The inorganic trivalent arsenic (AsIII) and pentavalent arsenic (AsV) for example are the most toxic arsenic forms, whereas the organic monomethyl arsenic (MMA) and dimethyl arsenic (DMA) have significantly reduced toxicities, while arsenobetaine (AsB) is not toxic at all.

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The application note describes a gradient method for the PQ LC HPLC system developed to separate five arsenic species with special attention to well separated chromatographic signals in shortest time. To test the method's applicability for real samples, commercially available apple juice and orange juice samples were analyzed.

Materials and Methods

Samples and Reagents

- Ammonium carbonate for preparation of Mobile Phase A and B
- Mobile Phase A–6.25 mM $(NH_4)_2CO_3$ and Mobile Phase B–60 mM $(NH_4)_2CO_3$
- Arsenic species: AsIII, AsV, MMA, DMA
- Internal standard: AsB

The calibration solutions were prepared in concentration ranges of 0.1, 0.5, 1, 5 and 10 µg/L for all arsenic species.
The apple juice and orange juice samples were diluted 1:1 with mobile phase A.

Instrumentation

The characterization of the samples was performed using a PQ LC HPLC system with autosampler, quaternary pump (metal free, PEEK) and column oven coupled to a PlasmaQuant MS ICP-MS (Table 1 and 2).

Table 1: Method settings for the PQ LC, HPLC system

Parameter	Settings
HPLC column	PRP-X100, 5 µm, 100 Å, PEEK, 4.6 X 150 mm
Mobile phase A	6.25 mM
Mobile Phase B	60 mM
Injection volume	50 µL
Flow rate	1.25 mL/min
Total run time	7 min

Table 2: Method settings for the PlasmaQuant MS, ICP-MS

Parameter	Settings
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.35 L/min
Nebulizer gas flow	0.97 L/min
iCRC settings	Hydrogen, 40 mL/min
Plasma RF power	1300 W
Dwell time	200 ms

The optimized LC gradient method (table 3) guarantees well-separated signals for the individual arsenic species in short analysis time. Since the method finishes with the initial setting of 100% mobile phase A, no extra stabilization or equilibration step was necessary.

Table 3: HPLC gradient method

Step	Time [min]	A [%]	B [%]	Flow [mL/min]
1	Initial	100	0.0	1.25
2	0.10	95.0	5.0	1.25
3	0.50	95.0	5.0	1.25
4	0.60	50.0	50.0	1.25
5	0.70	0.0	100	1.25
6	2.00	0.0	100	1.25
7	4.50	100	0.0	1.25
8	6.00	100	0.0	1.25
9	7.00	100	0.0	1.25

Results and Discussion

Arsenobetaine was used as internal standard for the whole experiment. The observed variation throughout all injections was less than 0.5%. Figures 1-4 show the excellent calibrations obtained between 0.1 and 10 µg/L with good linear correlations (Table 4).

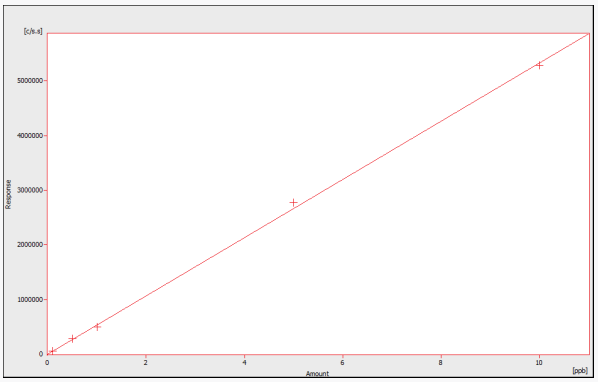

Figure 1: Calibration curve for AsIII

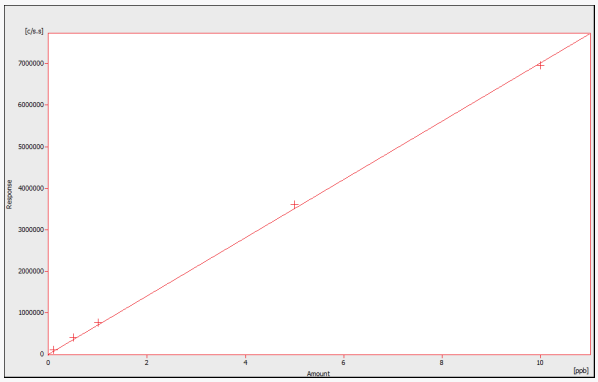

Figure 2: Calibration curve for AsV

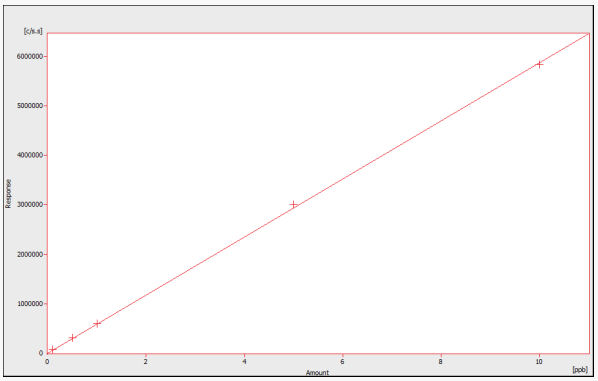

Figure 3: Calibration curve for MMA

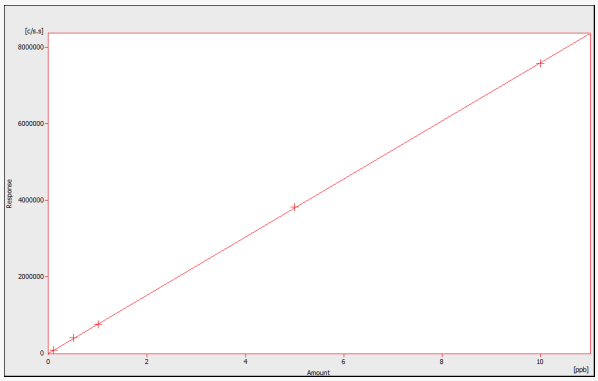

Figure 4: Calibration curve for DMA

The results obtained for the commercially available apple and orange juice are listed in Table 4. The respective chromatograms that underline the performance of the method are shown in Figure 5 and 6.

Table 4: Correlation coefficients for the calibration curves and results for commercial samples

Standard	R^2 calibration	Concentration [µg/L]	
		Apple Juice	Orange Juice
AsIII	0.9996983	0.348	0.110
DMA	0.9999857	0.039	0.036
MMA	0.9998867	0.019	0.032
AsV	0.9998668	1.360	0.482
Total As	-	1.776	0,660

AsV was the major species in both juice samples (Table 4). The apple juice contained about 1.8 µg/L total arsenic, mainly in inorganic form (Figure 5). With 0.66 µg/L the orange juice contained less total As but also mainly present as inorganic As (Figure 6). Both samples contained less than 2 µg/L total arsenic, which can be considered harmless. The current limit value of the Drinking Water Ordinance for Arsenic is 10 µg/L.

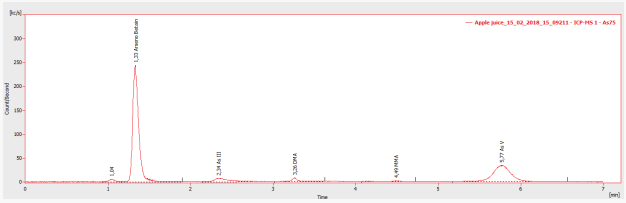

Figure 5: Chromatogram for As in Apple Juice

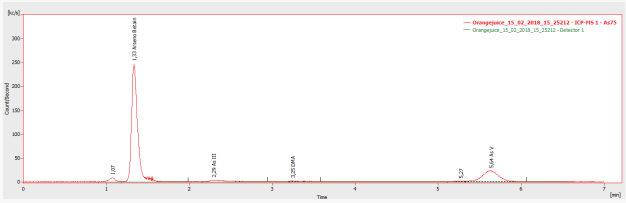

Figure 6: Chromatogram for As in Orange Juice

Conclusion

The developed method provides a robust and reliable tool for the identification of arsenic species in beverages. The obtained chromatograms for real samples reveal a stable performance with good match of internal standard (AsB) signals. Stable retention times and a clear separation within seven minutes underline the robustness of the method.

Combining the PQ LC, HPLC system with the PlasmaQuant MS, ICP-MS offers an easy and sensitive solution for the identification of arsenic species in food samples. The method is ideal for routine testing of arsenic species in foods such as beverages.

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