SPECIAL APPLICATION NOTE
PlasmaQuant® MS Elite

analytikjena

Speciation of arsenic in apple juice by LC-ICP-MS on PlasmaQuant® MS Elite

1. INTRODUCTION

The different physico-chemical forms of most elements vary in terms of mobility, toxicity and bioavailability. For example, arsenic species such as the inorganic trivalent arsenic (As III) and pentavalent arsenic (AsV) are highly toxic whereas the organic forms as monomethyl arsenic (MMA) and dimethyl arsenic (DMA) have significantly reduced toxicities. Reporting only the total concentrations can often be misleading.

When Liquid Chromatography (LC) is interfaced with Inductively Coupled Plasma Mass Spectrometry (ICP-MS), species elute one by one from the LC column directly to the ICP-MS for detection by elemental speciation. The coupling of LC to ICP-MS is a straight forward task; no hardware changes are required to either the LC or ICP-MS. The LC column is connected directly to the nebulizer of the ICP-MS. Coupling an LC to the PlasmaQuant® MS Elite has the added advantage of offering up to 5 times more sensitivity, offsetting the loss of total signal resulting from the separation of each species and providing very low part-per-trillion (ng/L) detection limits.

Fruits can be highly polluted with arsenic today, due to the use of arsenic-based pesticides during the past century. The following experiment shows the sensitivity and detection capabilities of the PlasmaQuant MS Elite for arsenic speciation in apple juice.

2. INSTRUMENTATION

The LC system used was a BRUKER Advance HPLC system with a 50 µm sample loop and a Hamilton PRP-X100 (4.6 mm x 150.0 mm, 5 µm) anion exchange column. The ASpect MS software allows automatic optimization of the ion optics and plasma gas flows. Prior to connecting the LC to the ICP-MS, it was optimized for maximum sensitivity on arsenic isotopes. ICP-MS and LC conditions are summarized in tables 1 and 2.

Table 1: PlasmaQuant® MS Elite ICP-MS operating conditions

Parameter	Settings
Plasma Gas Flow	9.0 L/min
Auxiliary Gas Flow	1.00 L/min
Nebulizer Gas Flow	1.00 L/min
Sheath Gas Flow	0.00 L/min
Plasma RF Power	1.30 kW
Monitored Ion	^{75}As
Scan Mode	Time Resolved
Dwell Time	500 ms
Pump Rate	25 rpm - black/black PVC pump tubing
Spraychamber Temp.	3 °C
Ion Optics	Optimized for ^{75}As sensitivity

Table 2: LC operating conditions

Parameter	Settings
Mobile Phase	A : 12.5 mM ammonium carbonate, 1 % MeOH B : 60.0 mM ammonium carbonate, 1 % MeOH
Flow Rate	1 mL/min
Run Time	12 min
Column	Anion exchange, Hamilton PRP-X100, 4.6 mm x 150.0 mm, 5 µm
Column Temperature	40 °C
Sample Injection	50 µL
Detection	PlasmaQuant® MS Elite ICP-MS

3. REAGENTS AND SAMPLES

Deionized water (18.2 MΩ/cm, Millipore MiliQ, Billerica, MA, USA) was used for all solution preparations (mobile phases, standard solutions and samples).

Mobile phase (LC)

Ammonium carbonate Puratronic® (Alfa Aesar) and methanol absolute ULC/MS (Biosolve BV, 5555 Valkenswaard) were used to produce both A (12.5 mM ammonium carbonate, 1 % MeOH) and B (60 mM ammonium carbonate, 1 % MeOH) mobile phases. Mobile phases were prepared daily.

Calibration standards

Calibration solutions of arsenic trioxide (AsIII, Acros Organics), arsenic pentoxide (AsV, Sigma-Aldrich), monosodium acid methane arsonate (MMA, Supelco) and cacodylic acid (DMA, Fluka) were prepared daily. Calibration ranged from 0.1 to 2.5 µg/l for all arsenic species

Sample preparation

Five different apple juices (Juice 1 to 5) were purchased in a French supermarket including an organically grown product (Juice 2). The samples were filtered using a 0.45 µm filter (Millipor Millex-HV) to suppress suspended matter. Filtrates were then diluted two-fold prior to analysis.

Internal standard

Arsenobetaine (BCR626, IRMM) was spiked in every solution (standard solutions and samples) at 1 µg/L to correct for any potential drift and matrix effect.

4. RESULTS AND DISCUSSION

Elemental speciation

Speciation of the four arsenic species (AsIII, DMA, MMA, AsV) and arsenobetaine (internal standard) were performed using the gradient LC method in less than 10 minutes. Excellent calibrations for each of the arsenic species were obtained with calibration coefficients ≥ 0.9999 achieved when calibrating on solutions ranging from 0.1 to 2.5 µg/L as illustrated in Figure 1.

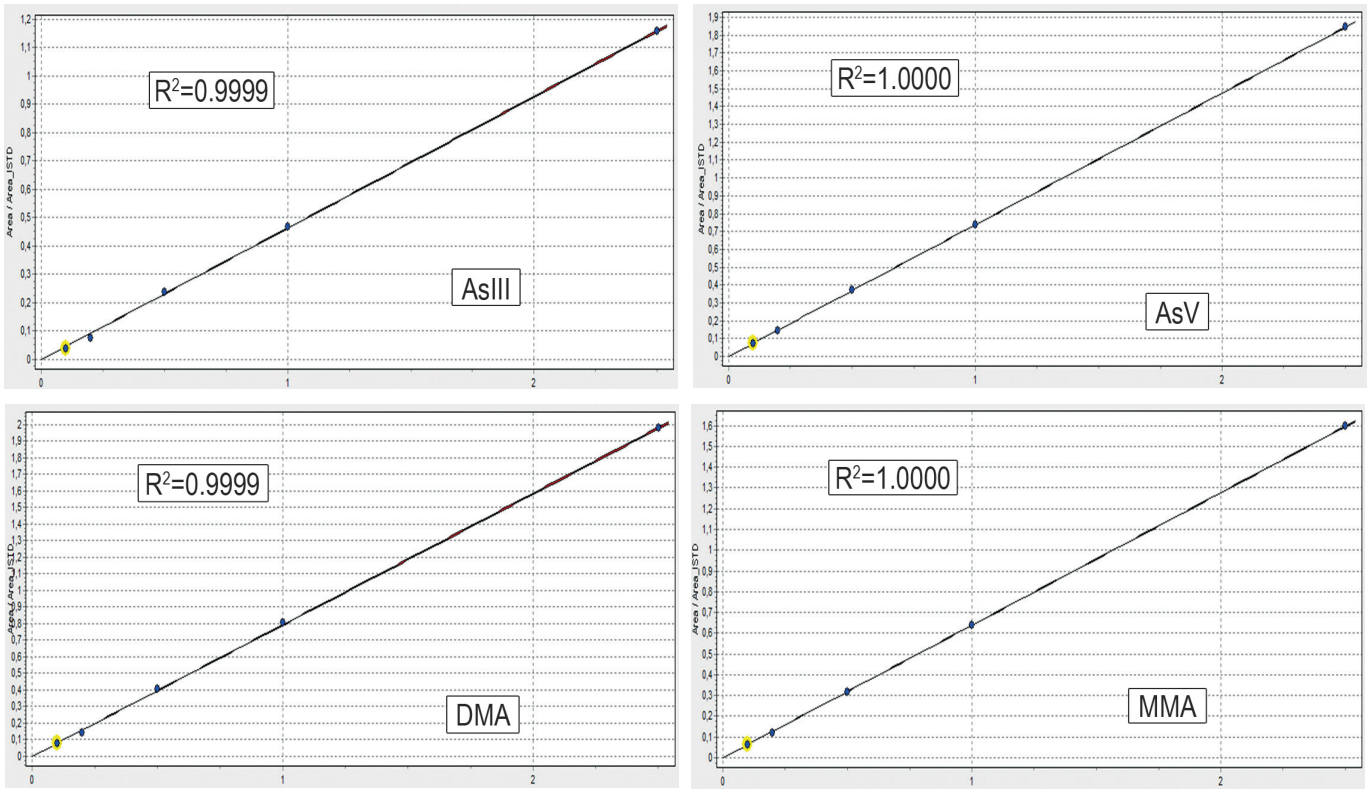

Figure 1: Calibration curves for AsIII, AsV, DMA and MMA

Apple juice analysis

Table 3 summarizes the As determination in five apple juice samples.

Table 3: As species concentration in five commercial apple juices

	Concentration (µg/L)				
	AsIII	DMA	MMA	AsV	**Total As**
Juice 1	0.297	0.088	0.010	1.550	**1.945**
*Juice 2	0.052	0.037	0.007	0.102	**0.198**
Juice 3	0.186	0.084	0.007	0.430	**0.707**
Juice 4	1.172	0.220	0.006	0.197	**1.595**
Juice 5	0.331	0.051	0.000	1.847	**2.229**

* Juice 2 was an organically grown product and had the lowest concentration of arsenic. The total As content in all five juices did not exceed 3 µg/L.

Spike recovery

To evaluate the repeatability of the method, undiluted apple juice 1 was spiked with 1ug/L of each species. The spiked sample was measured ten times and the average spike recovery for the four species is reported in table 4.

Table 4: Results of the spike recovery test

	Apple juice 1 + 1ug/L spike											
	Average concentration in the unspiked sample	Spiked samples										Average spike recovery
		1	2	3	4	5	6	7	8	9	10	
AsIII	0.297	1.254	1.236	1.210	1.244	1.184	1.244	1.228	1.190	1.184	1.210	92 %
DMA	0.088	1.022	1.000	0.966	1.018	0.966	1.018	1.004	0.972	0.962	0.998	90 %
MMA	0.010	0.918	0.900	0.884	0.952	0.884	0.936	0.918	0.884	0.904	0.898	90 %
AsV	1.550	2.548	2.538	2.440	2.602	2.448	2.608	2.566	2.480	2.512	2.474	97 %

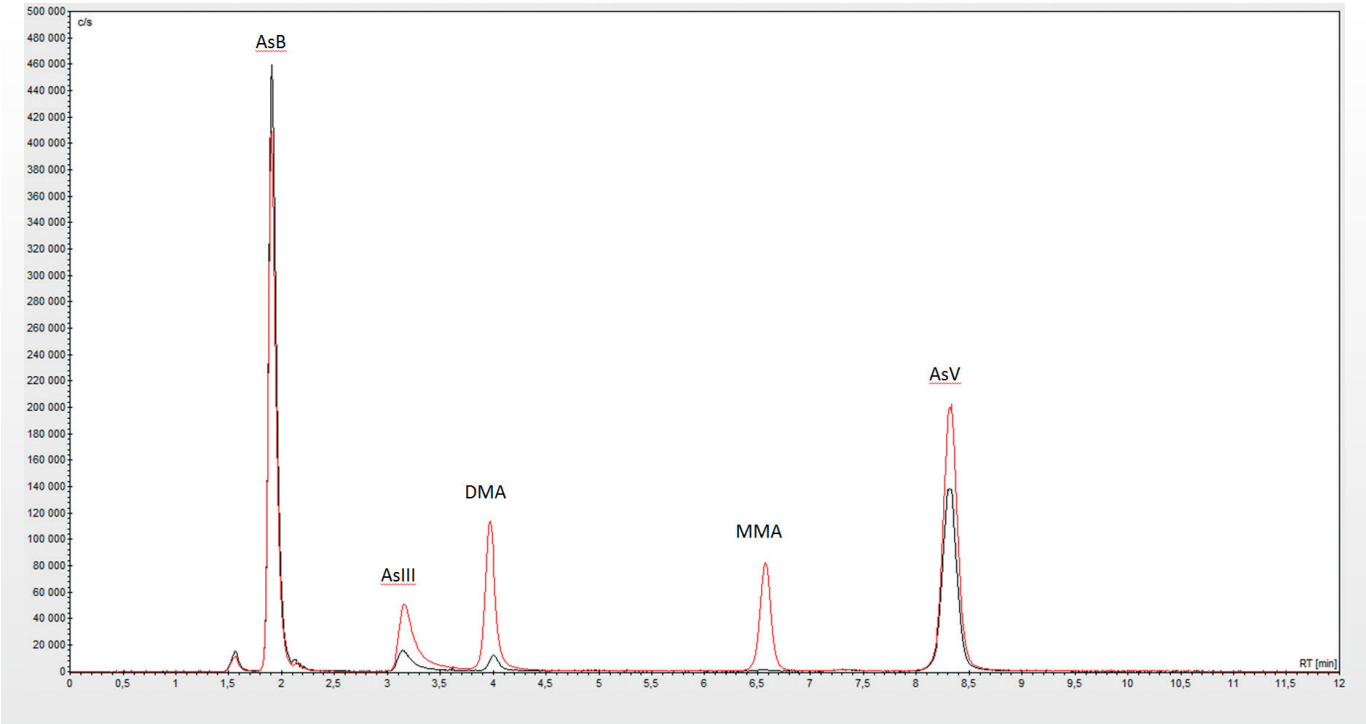

Figure 2: Overlay of 1 ug/L spiked (red) and unspiked (black) apple juice chromatograms

Long Term Stability

40 apple juice samples (8 hours) were run in the same sequence and a calibration check solution at 1 µg/L was measured every 10 samples. Table 5 summarizes the results.

Table 5: Robustness test using a 1 µg/L calibration check solution over a sequence of 40 samples (8 hours)

	AsIII (µg/L)	DMA (µg/L)	MMA (µg/L)	AsV (µg/L)
Check 1	1.021	1.031	1.012	1.024
Check 2	1.046	1.025	1.014	1.014
Check 3	1.024	1.029	1.001	1.000
Check 4	0.997	1.048	1.026	1.034

Typical detection limits

Table 6 shows the method detection limits (DLs) for the four common organic and inorganic forms of arsenic in apple juice. All the measurements were made under routine laboratory conditions.
Detection limits were calculated using 3 times the standard deviation of blank samples (n=10).

Table 6: Typical detection limits in apple juice using the PlasmaQuant® MS Elite

Arsenic species	Detection limit (ng/L)
Arsenite (AsIII)	2.7
Dimethyl arsenic acid (DMA)	2.6
Monosodium acid methane arsonate (MMA)	2.7
Arsenate (AsV)	3.3

5. CONCLUSION

This work has demonstrated that the PlasmaQuant® MS provides excellent detection capability when coupled with a BRUKER Advance HPLC system for arsenic speciation in apple juice. Minimal sample preparation is required and consists of simple filtration and a two-fold dilution. The high sensitivity of the PlasmaQuant® MS Elite allows for routine detection of arsenic species to low part per trillion (ng/L) levels.

Analytik Jena AG
Konrad-Zuse-Str. 1
07745 Jena/Germany
Phone: +49 (0) 36 41/77 70
Fax: +49 (0) 36 41/77 92 79
info@analytik-jena.com
www.analytik-jena.com