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Notes

Fast Determination of Toxic Arsenic Species in Food Samples Using Narrow-bore High-Performance Liquid-Chromatography Inductively Coupled Plasma Mass Spectrometry

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A new method for the speciation analysis of arsenic in food using narrow-bore high-performance liquid-chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) has been developed. Fast separation of arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid was carried out in 7 min using an anion-exchange narrow-bore Nucleosil 100 SB column and 12 mM ammonium dihydrogen phosphate of pH 5.2 as the mobile phase, at a flow rate of 0.3 mL min^{-1}. A PFA-ST micronebulizer jointed to a cyclonic spray chamber was used for HPLC-ICP-MS coupling. Compared with standard-bore HPLC-ICP-MS, the new method has provided higher sensitivity, reduced mobile-phase consumption, a lower matrix plasma load and a shorter analysis time. The achieved instrumental limits of detection were in the 0.3 – 0.4 ng As mL^{-1} range, and the precision was better than 3%. The arsenic compounds were efficiently (>80%) extracted from various food samples using a 1:5 methanol/water solution, with additional ultrasonic treatment for rice products. The applicability of this method was demonstrated by the analysis of several samples, such as seafood (fish, mussels, shrimps, edible algae) and rice-based products (Jasmine and Arborio rice, spaghetti, flour, crackers), including three certified reference materials.

Keywords Arsenic speciation, food analysis, narrow-bore column, Nucleosil SB

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Introduction

Arsenic speciation analysis of food products is a major analytical issue because of the wide-ranging levels of toxicity exhibited by the various chemical species of this element. In particular, arsenite (As^{III}) and arsenate (As^{V}) are highly toxic and carcinogenic to humans,[1] while monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) exhibit significantly lower toxicity[2] and arsenobetaine (AB) is basically non-toxic.[3]

Alongside water, food is the main contributor to the daily intake of total arsenic.[4,5] In many countries, the largest percentage of daily intake of arsenic comes from seafood, which can bio-accumulate a variety of mostly organic arsenicals and less inorganic arsenic.[6] A greater threat to human health comes from rice consumption, since it is a bio-accumulative plant for toxic inorganic species.[7-10] Therefore, arsenic speciation analysis of rice and seafood is greatly needed for risk assessment and food safety control, thus requiring fast, sensitive and reliable analytical methods, capable of separating and measuring individual arsenic species.[11]

Nowadays, the coupling of high-performance liquid chromatography (HPLC) to inductively coupled plasma mass spectrometry (ICP-MS) is the most commonly used technique for the speciation analysis of arsenic; it has been widely applied to determine inorganic and organic arsenic species in rice products,[13-18] wine,[19] seafood,[20-24] fruits[25] and cereal-based food.[26]

Despite these successful applications, the use of HPLC-ICP-MS for the routine arsenic speciation analysis of food samples still presents some limitations. In fact, the rapid and simultaneous determination of different arsenic compounds often requires high-salinity mobile phases or high values of the mobile phase flow rate.[11] These conditions may cause significant degradation of the stability and the ionization efficiency of the ICP source, the consumption of large volumes of reagents and extensive waste production.

One way to overcome these problems is to decrease the mass of the solution introduced into the spectrometer by working with small-bore columns,[27-29] which can provide faster separation and a lower mobile-phase flow rate than the conventional ones, and thus minimizing the matrix plasma load, reagents consumption and waste production. In this work, we present a new HPLC-ICP-MS method based on narrow-bore anion-exchange chromatography, able to provide fast and reliable determinations of toxic arsenic species in a large variety of food samples, including seafood and rice-based products.

Experimental

Instrumentation

The HPLC-ICP-MS system consisted of a Perkin Elmer-Sciex

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Series 200 HPLC, equipped with an autosampler and vacuum degasser, coupled to a Perkin Elmer-Sciex Elan DRC II. The interface between the HPLC and ICP-MS was selected according to the chromatographic liquid flow rate: (i) Mira Mist pneumatic nebulizer (Burgener Research Inc.)/glass cyclonic spray chamber (Perkin Elmer-Sciex) for conventional HPLC-ICP-MS and (ii) PFA-ST micronebulizer (Elemental Scientific)/low-volume Cinnabar spray chamber (Glass Expansion) for narrow-bore HPLC-ICP-MS. In the latter situation, a 11 × 0.026 cm i.d. transfer line was used to connect the output of the HPLC column to the PFA-ST nebulizer, leading to an extra column dead volume of about 6 µL; that is sufficiently low compared to that for the column (about 200 µL). The ICP-MS operated in DRC mode (oxygen) for total arsenic determination and in standard mode for speciation analysis. The operating conditions are reported as Supporting Information.

Standards, samples and certified reference materials

Standard solutions containing 1000 mg As L^{-1} of each of the following compounds were prepared in Milli-Q water (Merck Millipore): arsenate as $Na_2HAsO_4{\cdot}7H_2O$ (Merck); arsenite as $NaAsO_2$ (Merck), dimethylarsinate as $C_2H_6AsNaO_2{\cdot}3H_2O$ (Sigma-Aldrich) and methylarsonate as $Na_2CH_3AsO_3{\cdot}6H_2O$ (Chem Service). For the determination of arsenosugars, the reference algal sample by Madsen *et al.*[30] was used after the addition of 500 µL of Milli-Q water to the dry extract. Seafood products included canned and fresh tuna fish, mussels, kombu algae and shrimps, bought in a local fishery. Rice-based products, purchased in a local supermarket, comprised two types of white rice (Jasmine and Arborio) and some gluten-free products for celiac people, including two types of rice crackers, rice spaghetti and rice flour. Cracker #1 was mainly (99.7%) constituted of organic brown rice, while Cracker #2 was made by rice flour (90%), buckwheat (6%) and inulin (3%). For method validation, three certified reference materials were considered: TORT-2 (lobster hepatopancreas) from the National Research Council of Canada, SRM 1568a (rice flour) from the National Institute of Standards and Technology and MURST-ISS-A2 (Antarctic krill) from Istituto Superiore di Sanità (Italy).

Determination of total arsenic

The total arsenic concentrations in the samples were determined by ICP-MS after microwave-assisted acid digestion (details of the sample preparation procedure are reported as Supporting Information). The quantification was based on AsO^+ detection using acid-matching external calibration. The accuracy of the analytical procedure was verified by analyzing the certified reference materials: SRM 1568a (found concentration: 0.30 ± 0.01 mg kg^{-1}, n = 8; certified concentration: 0.29 ± 0.03 mg kg^{-1}), TORT-2 (found concentration: 23.7 ± 0.7 mg kg^{-1}, n = 3; certified concentration: 21.6 ± 1.8 mg kg^{-1}) and MURST-ISS-A2 (found concentration: 5.05 ± 0.08 mg kg^{-1}, n = 3; certified concentration: 5.02 ± 0.44 mg kg^{-1}). The total arsenic concentrations in the extracts were determined by ICP-MS after 10-fold dilution with Milli-Q water. The quantification was based on AsO^+ detection, by external calibration against arsenate standard solutions prepared in 2% (v/v) methanol.

Determination of arsenic compounds

Quantification of arsenic compounds was obtained by anion-exchange HPLC-ICP-MS after extraction by a 1:5 methanol/water solution, with additional ultrasonic treatment for rice products (details of the sample preparation procedure are reported as Supporting Information). Separations were performed on a Chronus Nucleosil 100 SB (100 × 2.1 mm i.d., 5 µm) narrow-bore column, using 12 mM aqueous $NH_4H_2PO_4$ (Merck) of pH 5.2 containing 2% (v/v) methanol, at a flow rate of 0.3 mL min^{-1}. The injection volume was 10 µL. For comparison purposes, anion-exchange separations were also performed using a Hamilton PRP X-100 (250 × 4.1 mm i.d., 10 µm) column. The mobile phase was 20 mM aqueous $NH_4H_2PO_4$ of pH 6 containing 2% (v/v) methanol, at a flow rate of 1.5 mL min^{-1}. The injection volume was 20 µL. The accuracy of the analytical procedure was verified by analysis of the certified reference materials (TORT-2, SRM 1568a and MURST-ISS-A2), obtaining values in good agreement with published data.[14-16,24,31-34]

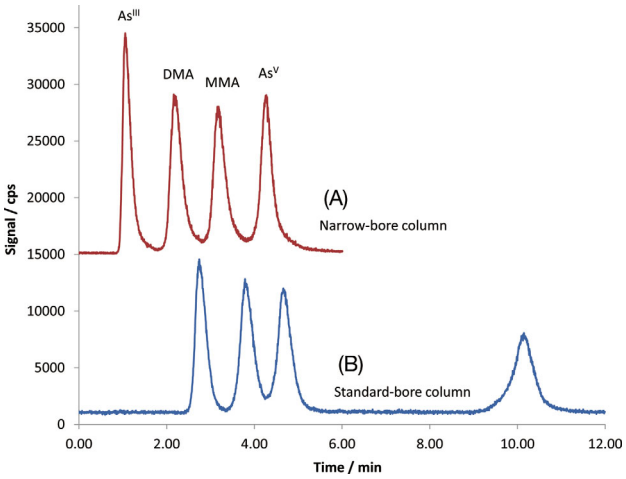

Fig. 1 Comparison of narrow-bore (A) and conventional (B) HPLC separation of As^{III}, As^V, DMA and MMA (50 ng As mL^{-1} each). (A) Column: Nucleosil (100 × 2.1 mm i.d., 5 µm); mobile phase: 12 mM $NH_4H_2PO_4$ of pH 5.2 + 2% (v/v) methanol; liquid flow rate: 0.3 mL min^{-1}. (B) Column: PRP X-100 (250 × 4.1 mm i.d., 10 µm); mobile phase: 20 mM $NH_4H_2PO_4$ of pH 6 + 2% (v/v) methanol; liquid flow rate: 1.5 mL min^{-1}.

Results and Discussion

Development of the HPLC-ICP-MS method

The retention behavior of the major toxic species of arsenic (As^{III}, As^V, MMA and DMA) on the narrow-bore anion-exchange Nucleosil 100 SB column was investigated by considering an aqueous solution of $NH_4H_2PO_4$ as the mobile phase (containing 2% methanol to increase the sensitivity)[35] and testing various combinations of the salt concentration (10 – 40 mM), pH (5.0 – 6.5) and liquid flow rate (0.2 – 0.5 mL min^{-1}). Optimal separation of the analytes was achieved using 12 mM $NH_4H_2PO_4$ of pH 5.2, at a flow rate of 0.3 mL min^{-1} (Fig. 1). The elution order followed the deprotonation properties of the compounds, analogously to conventional anion-exchange chromatography.[36]

The analytical performances of the narrow-bore HPLC-ICP-MS method were compared with those achieved using the conventional Hamilton PRP X-100 column, under the typical conditions.[11] The results are given in Table 1. By using a narrow-bore column, a shortening of the retention times was obtained, due to a reduction of the column length, and thus allowing separation of the studied arsenic species in less than 7 min, which is almost 2-times shorter compared to that for the

conventional column. The use of the narrow-bore column also led to an increase of the sensitivity, due to the higher analyte transport efficiency and the lower matrix plasma load resulting from the decrease in the mobile-phase flow rate. The latter condition was also favorable to minimize the mobile-phase consumption and to improve the long-term stability of ICP-MS.

The limits of detection (LODs) were computed as $3\sigma_b/m$, where σ_b and m are the standard deviation of the intercept and the slope of the calibration curve, respectively. The resulting LODs were in the 0.3 – 0.4 ng As mL^{-1} range, which are adequate for determining the investigated compounds in extracts from food samples, and comparable to previous studies.[11]

Linearity was assessed by analyzing standard solutions of the analytes, at different concentration levels (0, 10, 20, 50 and 100 μg L^{-1}). Mandel's fitting test based on a comparison of the standard error for a straight-line regression model with the standard error of a second-order polynomial regression model indicated that the latter did not provide a significantly better fit, at the 95% confidence level. The linear correlation coefficients were always higher than 0.9998. The precision of the chromatographic run was evaluated by ten consecutive injections of a standard solution containing a mixture of the arsenic compounds at a concentration of 20 ng As mL^{-1}. The relative standard deviation (RSD) was 2 – 3% in terms of both the peak area and the height. The precision of the whole analytical procedure was also very satisfactory, with the RSD ranging from <1% to 10% (n = 3), evaluated by the analysis of several real samples, as reported below.

Table 1 Comparison of narrow-bore and conventional HPLC-ICP-MS methods

Parameter	Compound	Narrow-bore HPLC-ICP-MS	Conventional method
Retention time (min)	As^{III}	1.4	1.7
	DMA	2.9	3.8
	MMA	4.2	5.0
	As^{V}	5.7	10.5
Calibration sensitivity (peak area/conc in ng mL^{-1})	As^{III}	7463	4951
	DMA	7725	5112
	MMA	7607	5357
	As^{V}	7819	5033
Detection limit (ng As mL^{-1})	As^{III}	0.3	0.3
	DMA	0.3	0.3
	MMA	0.4	0.9
	As^{V}	0.4	1.5

The possible co-elution of common arsenic species was explored by injecting standard solutions of arsenobetaine and arsenosugars 1 – 4[30] and recording the retention times. As expected, arsenobetaine eluted at the dead volume, potentially overlapping As^{III}. For seafood samples, which may contain significant amounts of arsenobetaine and/or other unretained cations, the presence of As^{III} was checked by oxidizing the extract with hydrogen peroxide (H_2O_2 1:10 (v/v), t >2 h, T = 23°C) to convert As^{III} to As^{V} and repeating the HPLC-ICP-MS analysis.[37] As regards arsenosugars, these compounds are differently retained by the chromatographic system, allowing for their determination.[29] In particular, arsenosugar 1 eluted with the front peak, while arsenosugar 2 eluted between DMA and MMA and its quantification was possible also in the presence of these compounds. The peak of arsenosugar 3 partially overlapped that of MMA, while arsenosugar 4 appeared after the complete elution of As^{V}.

Application to food samples

In order to illustrate the applicability of the developed method in the food-analysis field, various rice products and seafood samples were analyzed, and the results were compared with those obtained by the conventional HPLC-ICP-MS method (Tables 2 – 3). First, the arsenic mass balance at each stage of the analytical procedure was evaluated by determining the extraction yield and the HPLC column recoveries. The extraction yield was computed by ratioing the total arsenic concentration in the extract to the total arsenic concentration in the sample. For seafood products, the extraction procedure using 20% methanol was very efficient, leading to extraction yields in the 87 – 113% range. The precision of the extraction was 1 – 5% (RSD, n = 3). The same procedure also proved to quantitatively extract arsenic from some rice products, such as rice crackers and spaghetti, while significantly lower extraction yields were obtained for the rice flour samples (50 – 70%) and Arborio and Jasmine rice (30 – 40%). On the other hand, satisfactory extraction efficiencies (80 – 114%) were obtained by treating the rice samples in an ultrasonic bath for 6 h, in agreement with previous works.[38,39] The precision of the ultrasonic-assisted extraction was also good (RSD: 1 – 5%, n = 3). The column recoveries, calculated as the sum of the

Table 2 Arsenic speciation data for rice products

Sample	Method[a]	As^{III}	As^{V}	DMA	MMA	Total As[b]
Spaghetti	A	0.029 ± 0.001	0.014 ± 0.001	<0.003	<0.004	0.047 ± 0.001
	B	0.025 ± 0.001	<0.015	<0.003	<0.009	
Rice flour	A	0.077 ± 0.001	<0.004	0.011 ± 0.001	<0.004	0.119 ± 0.005
	B	0.079 ± 0.006	<0.015	0.011 ± 0.001	<0.009	
Cracker #1	A	0.053 ± 0.002	0.061 ± 0.002	0.028 ± 0.001	<0.004	0.125 ± 0.002
	B	0.058 ± 0.007	0.033 ± 0.004	0.031 ± 0.003	<0.009	
Cracker #2	A	0.113 ± 0.001	0.055 ± 0.001	0.046 ± 0.001	<0.004	0.227 ± 0.011
	B	0.142 ± 0.001	0.033 ± 0.001	0.033 ± 0.001	<0.009	
Jasmine rice	A	0.111 ± 0.001	<0.004	0.032 ± 0.001	<0.004	0.209 ± 0.003
	B	0.101 ± 0.005	<0.015	0.035 ± 0.001	<0.009	
Arborio rice	A	0.106 ± 0.004	0.010 ± 0.001	0.032 ± 0.002	<0.004	0.187 ± 0.001
	B	0.092 ± 0.007	<0.015	0.028 ± 0.001	<0.009	
SRM 1568a	A	0.076 ± 0.002	0.040 ± 0.002	0.189 ± 0.001	0.014 ± 0.002	0.299 ± 0.012[c]
	B	0.056 ± 0.004	0.039 ± 0.003	0.157 ± 0.001	0.018 ± 0.002	

Values are in μg As g^{-1} dry mass (mean ± SD, n = 3). a. Method A: narrow-bore HPLC-ICP-MS; method B: conventional HPLC-ICP-MS (see Experimental for details). b. Total arsenic concentration in the sample. c. n = 8.

Table 3 Arsenic speciation data for seafood products

Sample	Method[a]	As^{III}	As^{V}	DMA	MMA	Arsenosugar			Total As[b]
						1	**2**	**3**	
Mussel	A	<0.02	<0.02	0.32 ± 0.04	0.43 ± 0.03	nd[c]	0.36 ± 0.03	<0.02	16.4 ± 0.1
	B	<0.02	<0.07	0.35 ± 0.02	0.39 ± 0.02	nd[c]	nd[c]	<0.02	
Kombu algae	A	<0.02	<0.02	nd[c]	<0.02	6.3 ± 0.2	12.7 ± 0.3	41 ± 2	63 ± 3
	B	<0.02	<0.07	0.20 ± 0.01	<0.04	5.5 ± 0.1	10.7 ± 0.2	38 ± 1	
MURST-ISS-A2	A	<0.02	0.17 ± 0.01	0.14 ± 0.01	<0.02	nd[c]	0.28 ± 0.01	<0.02	5.05 ± 0.08
	B	<0.02	<0.07	0.16 ± 0.01	<0.04	nd[c]	0.30 ± 0.02	<0.02	
TORT-2	A	<0.02	0.64 ± 0.02	1.39 ± 0.05	<0.02	nd[c]	0.51± 0.01	<0.02	23.7 ± 0.7
	B	<0.02	0.63 ± 0.01	1.46 ± 0.09	<0.02	nd[c]	0.46 ± 0.03	<0.02	

Values are in μg As g^{-1} dry mass (mean ± SD, n = 3). a. Method A: narrow-bore HPLC-ICP-MS; method B: conventional HPLC-ICP-MS (see Experimental for details). b. Total arsenic concentration in the sample. c. Not determined due to a chromatographic interference.

arsenic species eluted from the column divided by the total arsenic in the injected extract, were in the 70 – 110% range, thereby indicating a good overall recovery of the arsenic species from the chromatographic system.

The analytical results reported in Tables 2 – 3 collectively indicate that the data obtained by the narrow-bore and conventional HPLC-ICP-MS systems are not significantly different (paired t-test, p <0.05), thus providing confidence in the developed method.

The rice products contained levels of arsenic below 0.3 μg g^{-1}, basically as As^{III}, As^{V} and DMA, that account for >80% of the total extracted arsenic. Arsenite was the predominant specie in rice flour (80%), spaghetti (67%), Arborio (66%) and Jasmine (63%) rice, and a major compound in crackers samples (37 – 48%). Arsenate mainly occurred in crackers (23 – 43%), while it was below the LOD in rice flour and Jasmine rice. DMA was detected in all samples (except spaghetti), representing about 20% of the total extracted arsenic and the major arsenic compound (58%) in the SRM 1568a. This reference material also presented the lowest percentage of inorganic arsenic (35%) and detectable concentration of MMA.

HPLC-ICP-MS chromatograms for tuna fish and shrimps only presented a large front peak due to the unretained cation species. In fact, the corresponding arsenic concentration values were in good agreement with the arsenobetaine content previously determined by cation-exchange chromatography (1.7 ± 0.1, 4.4 ± 0.1 and 169 ± 11 μg g^{-1}, for canned tuna, fresh tuna and shrimps, respectively). The other seafood samples also contained large amounts of cations, besides detectable concentrations of toxic species, mainly DMA and MMA. The former was found in mussels, kombu algae and CRMs, although it represented only 2 – 6% of the total extracted arsenic. MMA was only detected in mussels, at similar concentration as DMA. As^{V} was generally below the LOD (except in TORT-2), as was As^{III}, whose presence was ruled out by treating the extract with hydrogen peroxide and repeating the HPLC-ICP-MS analysis. Seafood samples also contained arsenosugars, mainly kombu algae (82% of total arsenic) and CRMs.

Conclusions

The use of narrow-bore HPLC-ICP-MS in conjunction with a low sample consumption system allows for the fast determination of toxic arsenic species in food samples, with adequate sensitivity and precision. Compared with conventional HPLC-ICP-MS, the new method provides higher sensitivity, a shorter analysis time, a reduced mobile phase consumption and minor matrix loading into the plasma source and the interface region of the ICP mass spectrometer. Therefore, the new method could represent a good option for routine food safety control, as demonstrated by analyses of various types of seafood and rice products.

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Supporting Information

ICP-MS operating conditions and details on sample preparation are available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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