JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Application of HPLC-ICP-MS and HPLC-ESI-MS Procedures for Arsenic Speciation in Seaweeds

Yu-Jhe Hsieh[†] and Shiuh-Jen Jiang*[,†,§]

[†]Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

[§]Department of Medical Laboratory Science and Biotechnology, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

Supporting Information

ABSTRACT: Speciation of arsenic in seaweeds was carried out using ion chromatography (IC) for separation and inductively coupled mass spectrometry (ICP-MS) for detection. The arsenic species studied were arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and arsenocholine (AsC). Chromatographic separation of all the species was achieved in <9 min in gradient elution mode using $(NH_4)_2CO_3$ and methanol at pH 8.5. The outlet of the IC column was directly connected to the nebulizer of ICP-MS for the determination of arsenic. The speciation of arsenic has been carried out in several seaweed samples. A microwave-assisted extraction method was used for the extraction of arsenic species from seaweed samples. With a mixture of mobile phase A and methanol as extractant, the extraction efficiency was >84%, and the recoveries from spiked samples were in the range of 90−106%. The unknown compounds detected in different seaweeds were identified by coupling IC directly with electrospray ionization−mass spectrometry (ESI-MS). Two arsenosugars and tetramethylarsonium ion (TETRA) were identified in different seaweeds. A fat-soluble arsenolipid compound was identified in the extract of certified reference material BCR-279 *Ulva lactuca* when 1% HNO_3 was used as the extractant. The precision between sample replicates was >9% for all determinations. The limits of detection were in the range of 0.006−0.015 $\mu g\ L^{-1}$ for various arsenic species based on peak height.

KEYWORDS: *arsenic speciation analysis, seaweed, ion chromatography, inductively coupled plasma mass spectrometry, electrospray ionization−mass spectrometry, microwave-assisted extraction*

INTRODUCTION

Arsenic is an analyte of high concern in the scientific community due to its toxic properties. It is very well-known that toxicity depends not only on the concentration but also on the chemical species in which this analyte is present.[1] The LD_{50} values of arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenocholine (AsC) and arsenobetaine (AsB) are 14, 20, 700−1800, 700−2600, 6500, and >10000 mg kg^{-1}, respectively.[2] Reviews by Le et al.[3] and McSheehy et al.[4] dealt with arsenic speciation and its accepted techniques, respectively. Arsenic is abundant in seafood at concentrations as high as several hundred micrograms per gram.[3] Therefore, in some countries, such as Japan, Korea, China, and Taiwan, where food from marine sources constitutes an important part of the diet, it is essential to know the concentrations of individual arsenic species to realize the level of toxicity. Several methods based on high-performance liquid chromatography (HPLC), ion chromatography (IC), and capillary electrophoresis (CE) coupled with different detection methods have appeared in the literature for arsenic speciation analysis in various samples.[5−14] Coupling of LC to ICP-MS gained much attention due to its ease of sample preparation, simplicity of interface to the detector, and specificity of the signal intensity of the determined element.[15] The aim of the present work is to develop a simple and accurate method for the speciation analysis of arsenic in different types of seaweed samples using IC-ICP-MS. The speciation analysis of arsenic in seaweed samples not only provides an idea about the level of toxicity but also gives information about which species is predominant in which type of seaweed. For the speciation analysis sample preparation is an important issue as the species need to be extracted from solid sample into a suitable extractant without altering the species. Microwave-assisted digestion gained wide acceptance as a rapid method for sample decomposition for inorganic analysis. Recently, it has also been verified as an appropriate tool for rapid preparation of solid samples for organometallic speciation analysis.[16−18] In this study, the microwave-assisted extraction method was used for the extraction of arsenic compounds in several seaweed samples.

Separations with HPLC coupled with inductively coupled plasma mass spectrometry (ICP-MS) allow one to fractionate the different arsenic-containing compounds and to measure the arsenic concentration of the different compounds. Matching their chromatographic retention times with those of standards allows their identification, but unfortunately not all compounds are available as calibration standards.[19] Detection of the different arsenic species by using ICP-MS is generally accepted as the most powerful method, although it gives only elemental information. Moreover, there is a possibility of misinterpretation if two species have the same retention time. Electrospray ionization−mass spectrometry (ESI-MS) provides molecular and structural verification of the compounds. Consequently, the use of ESI-MS is gaining importance in the field of speciation. In recent years some studies have used ESI-MS for achieving

Received: November 10, 2011
Revised: February 15, 2012
Accepted: February 17, 2012
Published: February 17, 2012

Table 1. Equipment and Operating Conditions

ICP-MS instrument	Perkin-Elmer SCIEX ELAN 6100 DRC II
ICP parameters	
RF power	1100 W
plasma gas flow rate	15.0 L min^{-1}
auxiliary gas flow rate	1.325 L min^{-1}
nebulizer gas flow rate	a L min^{-1}
mass spectrometer settings	
resolution	0.7 amu at 10% peak maximum
dwell time	50 ms
scan mode	peak hopping
sweeps/reading	5
readings/replicate	600
replicates	1
auto lens	on
isotope monitored	m/z 75 (As), m/z 77 ($^{40}Ar^{37}Cl$, ^{77}Se), m/z 35 (Cl)
HPLC system with ICP-MS	
pump	Hitachi model L-6000 Hitachi model L-6100 (Intelligent pump)
injector	Rheodyne 7125
stationary phase	Hamilton PRP-X100 anion exchange column 10 μm diameter particles 4.1 mm i.d. × 250 mm length
mobile phase	A: 0.5 mM ammonium carbonate, 1% MeOH (pH 8.5) B: 50 mM ammonium carbonate, 1% MeOH (pH 8.5)
gradient program	0−0.1 min 100% A ramp to 100% B; 0.1−8 min 100% B
mobile phase flow rate	1 mL min^{-1}
sample loop volume	100 μL
HPLC system with ESI-MS	
pump	Hitachi model L-2130
injector	Rheodyne 7725i
sample loop volume	20 μL
ESI-MS instrument	Bruker amaZon SL
ESI-MS parameters	
dry temperature	200 °C
nebulizer gas	15 psi (online) 5 psi (off-line)
drying gas	8 L min^{-1} (online) 3 L min^{-1} (off-line)
capillary voltage	−4500 V (positive mode)
accumulation time	100 ms
scan range	m/z 70−600
MRM amplitude	1.0 for arsenosugar 0.4 for AsC 0.6 for AsB 1.0 for TETRA 1.3 for arsenolipid

molecular and structural information on arsenosugars.[20−23] In this study an HPLC-ESI-MS method was used to determine several arsenic compounds in seaweed without standards.

MATERIALS AND METHODS

Equipment and Operating Conditions. An ELAN 6100 DRC II ICP-MS (Perkin-Elmer SCIEX, Concord, ON, Canada) was used for these experiments. Samples were introduced by a cross-flow pneumatic nebulizer with a Scott-type spray chamber. The operating conditions of ICP-MS were optimized by continuous introduction of a tune solution containing 1 μg L^{-1} As in mobile phase. The solution flow rate was maintained at about 1.0 mL min^{-1}. The ICP-MS operating conditions used in this work are summarized in Table 1.

The IC system includes two HPLC pumps (Hitachi, models L-6000 and L-6100), an injector (Rheodyne 7125), and an ion exchange column (Hamilton PRP-X100, 10 μm particle diameter, 4.1 mm i.d. × 250 mm length). Samples were loaded with a syringe onto a 100 μL sample loop. The operating conditions of ion chromatography used in this work are summarized in Table 1. The column outlet was connected to the pneumatic nebulizer of the ICP-MS device through polytetrafluoroethylene (PTFE) tubing (0.18 mm i.d. × 470 mm length).

The HPLC-ESI-MS/MS system used consisted of a Hitachi model L-2130 HPLC pump and an amaZon SL ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany). The mass spectrometer was equipped with an electrospray interface as the ionization source, which was operated under the conditions indicated in Table 1.

Chemicals. Analytical reagent grade chemicals were used without further purification. Purified water (18.2 MΩ·cm), from a Milli-Q

water purification system (Millipore, Bedford, MA, USA), was used to prepare all of the solutions. Dimethylarsinic acid, sodium arsenite(III), and ammonium carbonate were obtained from Sigma (St. Louis, MO, USA). Methanol, As(V) standard solution, and Suprapur nitric acid (65%) were purchased from Merck (Darmstadt, Germany). Arsenobetaine (AsB) was obtained from BCR (Brussels, Belgium) as a solution of AsB in water (BCR CRM 626, 1031 ± 6 mg kg^{-1}). Arsenocholine was obtained from Argus Chemicals (Vernio, Italy). Disodium methyl arsenate was from ChemService (West Chester, PA, USA). Stock solutions (1000 mg L^{-1}) of all arsenic species were prepared in pure water and diluted appropriately before use.

Sample Preparation and Extraction. The developed procedure was applied for the speciation of arsenic in several seaweed samples such as *Undaria pinnatifida*, *Laminaria japonica*, *Sargassum cristaefolium*, and *Porphyra dentata*, obtained locally. The accuracy of the procedure was verified by analyzing a certified reference material BCR-279 *Ulva lactuca* (Institute for Reference Materials and Measurements, Geel, Belgium). The BCR-279 *Ulva lactuca* is certified for total arsenic. A microwave-assisted extraction procedure was used for the extraction of arsenic species from seaweed samples. A CEM MARS (CEM, Matthews, NC, USA) microwave digester was used in this study. Seaweed samples (0.500 g each) were weighed into 15 mL polyethylene centrifuge tubes, and 5 mL of mobile phase A and 5 mL of methanol were added. The tubes were then put into a 500 mL beaker having 200 mL of water and exposed to microwave heating. The microwave system was programmed to maintain the temperature at 60 °C for 20 min with a ramp time of 10 min. After microwave heating, the solutions were allowed to cool and directly centrifuged for 10 min at 3743*g* (MIKRO 22R, Hettich, Germany). The supernatants were diluted to appropriate volumes and filtered through a PVDF filter (Pall Corp., Ann Arbor, MI, USA) of 0.2 μm porosity before IC separation. The concentration of arsenic species was determined by external calibration method based on peak area. The recovery was determined by spiking 0.5 g of a seaweed sample (0.25 g for *S. cristaefolium*) with appropriate amounts of arsenic standards and then extracted by the mixture of methanol and mobile phase A.

As the real world samples are not certified, to check the extraction efficiency of arsenic, the total concentrations of arsenic in the samples were determined, after complete dissolution of seaweed samples. The dissolution of the samples was carried out in a closed vessel at 80 psi using HNO_3. To approximately 0.5 g of samples taken in a PTFE vessel was added 5 mL of HNO_3, and the vessel was closed. The vessel was then heated at 60, 80, and 100 psi for 10 min each. The digest was diluted to 10 mL and analyzed by pneumatic nebulization ICP-MS with 1 μg L^{-1} of rhodium as the internal standard. These results were compared with thaose obtained by IC-ICP-MS method.

RESULTS AND DISCUSSION

Selection of Ion Chromatography Operating Conditions. The separation of six arsenic species, namely As(III), As(V), MMA, DMA, AsC, and AsB, was attempted by using an ion exchange column with $(NH_4)_2CO_3$ as mobile phase.[24] In this study, conditions similar to the previous work were selected. A gradient elution using 0.5 mmol L^{-1} and 50 mmol L^{-1} $(NH_4)_2CO_3$ in 1% v/v methanol at pH 8.5 was carried out, and the gradient program was 100% 0.5 mmol L^{-1} $(NH_4)_2CO_3$, ramp to 100% 50 mmol L^{-1} $(NH_4)_2CO_3$ from 0 to 0.1 min, 100% 50 mmol L^{-1} $(NH_4)_2CO_3$ from 0.1 to 8 min, and 100% 0.5 mmol L^{-1} $(NH_4)_2CO_3$ from 8 min until completion of the experiment. A typical chromatogram of a solution containing 5 μg L^{-1} (as element) of As(III), As(V), MMA, DMA, AsB, and AsC is shown in Figure 1a. As shown, all six species studied were well separated in <9 min. Furthermore, as shown in Figure 1b, the elution peak caused by $ArCl^+$, which might interfere with the determination of arsenic, was well separated from As(V) and MMA. The IC operating conditions used in this work are listed in Table 1. Repeatability was determined

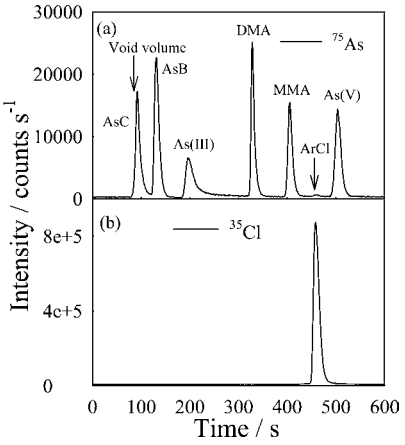

Figure 1. Typical element-selective chromatogram for (a) 5 ng mL^{-1} (as element) each of AsC, AsB, As(III), DMA, MMA, and As(V) and 100 mg L^{-1} of Cl^{1-} and (b) 100 mg L^{-1} of Cl^{1-}. IC conditions are given in Table 1.

using five consecutive injections of a test mixture containing 5 μg L^{-1} each of the six arsenic species studied. The relative standard deviation of the peak areas was <3%, and the repeatability of the retention time was >2% for all species. Calibration curves (five points) based on peak heights and peak areas were linear with correlation coefficient (r) >0.9996 for each species in the range studied (0.05−10 μg L^{-1}). From the experiment results, we found that the calibration sensitivities of various arsenic species based on peak area were similar. The detection limit was estimated from the peak height versus concentration plot and based on the concentration (as element) necessary to yield a net signal equal to 3 times the standard deviation of the background. The IC-ICP-MS detection limita were 0.007, 0.007, 0.015, 0.006, 0.009, and 0.011 μg L^{-1} for AsC, AsB, As(III), DMA, MMA, and As(V), respectively. The detection limits of various arsenic species obtained in this work are better than or comparable to previous results with similar techniques.[7−11,24−26]

Extraction of Arsenic from Seaweeds. For the extraction of arsenic species from seaweed samples, various solutions, namely, 1% v/v HNO_3, mobile phase A, 1% v/v HNO_3 in mobile phase A, and a mixture of 50% methanol and 50% mobile phase A, were tested as the extracting solutions at the extraction temperature of 60 °C for 20 min with a ramp time of 10 min by microwave heating. From the experiments it was found that better extraction efficiency could be obtained when 1% HNO_3 in mobile phase A or a mixture of 50% methanol and 50% mobile phase A was used as the extracting solution. As reported by Foster et al.,[27] the addition of HNO_3 in the extraction solution could facilitate the extraction of arsenic from marine plant and animal tissues. However, to get better IC chromatogram and to avoid the degradation of arsenic compounds, in the following experiments, a mixture of 50% methanol and 50% mobile phase A was selected as the extracting solution. The effect of the extraction temperature on extraction efficiency was studied at 50, 60, 70, and 80 °C. It was found that the extraction efficiency did not change significantly with the temperature. An extraction temperature of 60 °C was selected for the following experiments. The total concentrations of arsenic in the extracts were determined by IC-ICP-MS. As shown in Tables 2 and 3, under the conditions selected, the extraction efficiency of arsenic species was >89% for all types of seaweed samples, whereas it was 84% for BCR-279.

Arsenic Speciation Analysis in Seaweed Samples. To check the applicability of the reported procedure for routine

dx.doi.org/10.1021/jf204595d | J. Agric. Food Chem. 2012, 60, 2083−2089

Table 2. Recoveries and Concentrations of Arsenic Species in BCR-279, As Measured by IC-ICP-MS[a] (n = 3)

compound	BCR-279	
	concn found/μg g^{-1}	recovery/%
AsC	nd[b]	97 ± 1
AsB + OH-arsenoribose + TETRA	1.07 ± 0.012	102 ± 2
As(III)	0.065 ± 0.003	94 ± 2
DMA	0.200 ± 0.004	98 ± 3
PO_4-arsenoribose	0.302 ± 0.008	
MMA	0.234 ± 0.010	91 ± 3
As(V)	0.674 ± 0.022	98 ± 2
sum of species	2.55 ± 0.05 (84%)[c]	
total[d]	3.02 ± 0.12	
certified value	3.09 ± 0.21	

[a]Values are the mean of three measurements ± standard deviation. [b]nd, not detected. [c]The extraction efficiency was compared with the total arsenic concentration. [d]Determined by ICP-MS after microwave digestion.

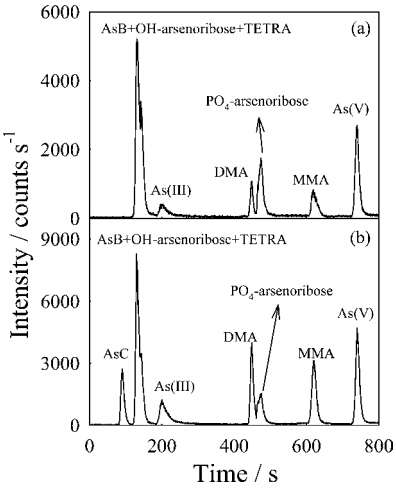

Figure 2. Typical chromatogram of (a) the extract of BCR-279 *Ulva lactuca* and (b) BCR-279 *Ulva lactuca* spiked with 0.04 μg g^{-1} each of the arsenic standards. The concentrations of DMA and As(V) in injected solution were 0.5 and 1.7 μg L^{-1}, respectively.

monitoring of arsenic species in seaweed samples, four different seaweeds purchased from the local market and a reference sample BCR-279 *Ulva lactuca* were analyzed for arsenic compounds. The extraction of arsenic species of interest in seaweed samples has been carried out by using a mixture of 5 mL of methanol and 5 mL of mobile phase A at 60 °C for 20 min. A 100 μL injection of the extract of seaweed was analyzed for As species using the IC-ICP-MS method. The typical chromatogram for BCR-279 recorded at m/z 75 is shown in Figure 2. To get better resolution, in this separation the ramp time of the IC gradient elution was increased from 0.1 to 8 min for BCR-279 extracts. As shown in Figure 2, except for AsC, various arsenic species studied in this work are present in this sample. Several unknown major peaks appeared in the BCR-279 extract, but could not be identified by analyte addition method due to the lack of suitable standards. In this study the unknown compounds were identified online by IC-ESI-MS. As shown in Figure 3, three major compounds were coeluted at about 130 s. Furthermore, another major peak at m/z 483 was detected at 265 s. As shown in Figure S1 (Supporting Information), the compounds were identified to be tetramethylarsonium ion (TETRA), AsB, OH-arsenoribose, and PO_4-arsenoribose using ESI-MS/MS. The retention times of the elution peaks were different slightly from IC-ICP-MS results due to the difference in the interface system. Although not shown in the text, the chromatogram has been monitored for a longer time, and no OSO_3H-arsenoribose and SO_3H-arsenoribose were detected in the extracts of the seaweed samples analyzed in this work. As shown in Table 2, the extraction efficiency of arsenic species in BCR-279 was only 84%. The residue of the BCR-279 sample after microwave extraction was extracted with 1% v/v HNO_3 at 90 °C for 20 min and centrifuged, and then the supernatant was introduced into ICP-MS for arsenic determination. Fourteen percent of total arsenic was detected in the HNO_3 extract. The extract was also introduced into ESI-MS directly with a syringe pump. It is interesting to see that a major peak was detected at m/z 437. As shown in Figure 4, the compound could be dimethylarsinoyl fatty acid (arsenolipid) previously reported using ESI-MS/MS,[28,29] which needs further identification using high-resolution ESI-MS/MS.

The method developed was also applied to determine arsenic compounds in four types of seaweed samples obtained locally. The chromatograms of the extracts of seaweed samples recorded at m/z 75 are shown in Figures S2–S5 (Supporting Information). From the experiments it was found that the major arsenic compounds in the seaweeds varied significantly. OH-arsenoribose was the major arsenic compound in *Undaria pinnatifida*, *L. japonica*, and *S. cristaefolium*. Instead, PO_4-arsenoribose was the major arsenic-containing compound in *P.*

Table 3. Recoveries and Concentrations of Arsenic Species in Seaweed Samples, As Measured by IC-ICP-MS[a] (n = 3)

compound	*Undaria pinnatifida*		*Laminaria japonica*		*Sargassum cristaefolium*		*Porphyra dentata*	
	concn found/μg g^{-1}	recovery/%	concn found/μg g^{-1}	recovery/%	concn found/μg g^{-1}	recovery/%	concn found/μg g^{-1}	recovery/%
AsC	nd[b]	98 ± 1	nd	105 ± 1	nd	98 ± 3	nd	94 ± 3
AsB	nd	96 ± 2	nd	92 ± 3	nd	95 ± 2	nd	106 ± 2
OH-arsenoribose	22.0 ± 0.3		23.7 ± 0.8		2.42 ± 0.08		0.343 ± 0.022	
As(III)	nd	92 ± 4	nd	98 ± 1	0.152 ± 0.011	94 ± 4	nd	101 ± 3
DMA	1.30 ± 0.10	101 ± 2	0.571 ± 0.008	104 ± 4	0.432 ± 0.022	103 ± 4	0.235 ± 0.007	97 ± 2
PO_4-arsenoribose	nd		7.06 ± 0.15		0.834 ± 0.044		27.3 ± 0.2	
MMA	0.222 ± 0.020	91 ± 3	nd	101 ± 1	nd	99 ± 3	0.250 ± 0.003	90 ± 4
As(V)	nd	97 ± 2	nd	103 ± 3	0.533 ± 0.030	104 ± 4	nd	96 ± 2
sum of species	23.5 ± 0.3 (96%)[c]		31.3 ± 0.8 (96%)[c]		4.37 ± 0.13 (92%)[c]		28.1 ± 0.2 (89%)[c]	
total[d]	24.4 ± 0.8		32.6 ± 0.2		4.73 ± 0.09		31.6 ± 0.3	

[a]Values are the mean of three measurements ± standard deviation. [b]nd, not detected. [c]The extraction efficiency was compared with the total arsenic concentration. [d]Determined by ICP-MS after microwave digestion.

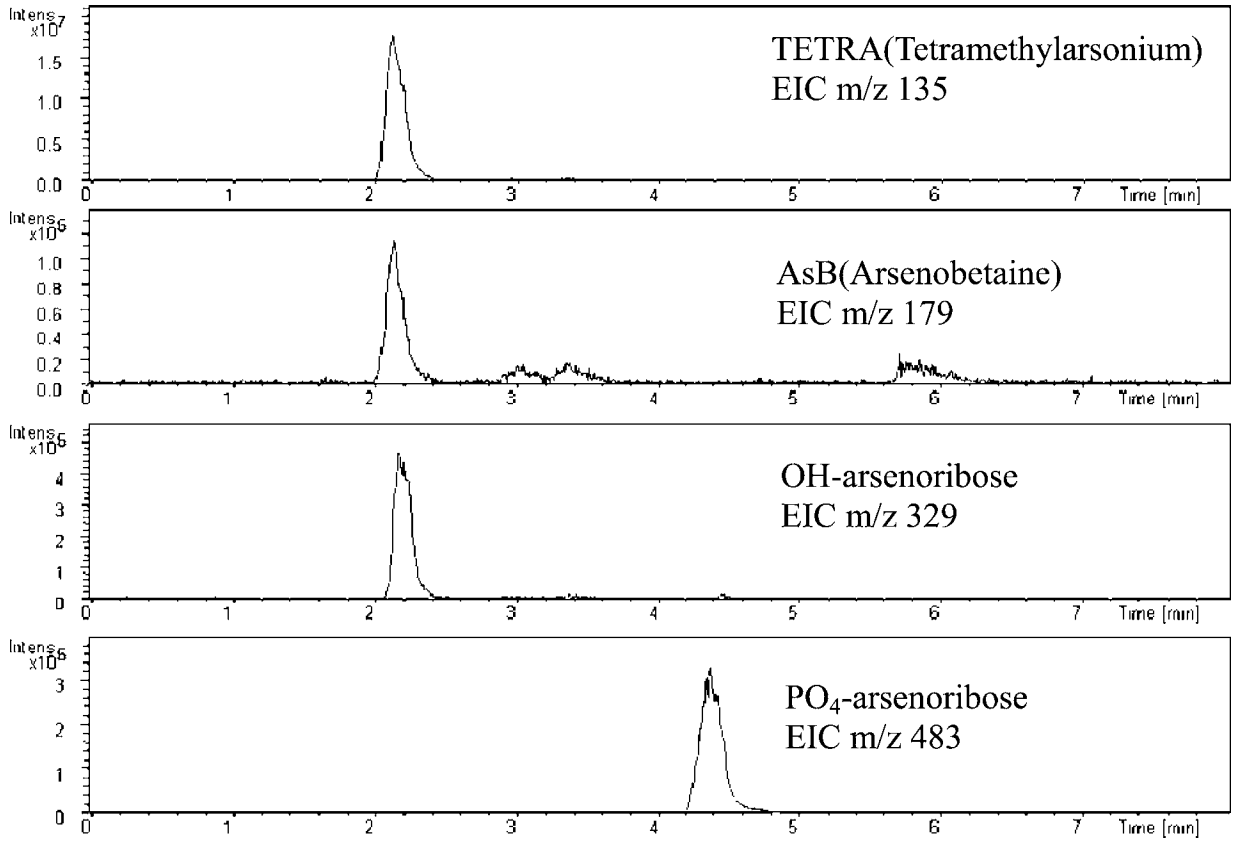

Figure 3. Ion exchange HPLC-ESI-MS chromatogram in EIC (extracted ion chromatogram) mode of BCR-279: (a) *m/z* 135 (TETRA); (b) *m/z* 179 (AsB); (c) *m/z* 329 (OH-arsenoribose OH-arsenoribose); (d) *m/z* 483 (PO_4-arsenoribose).

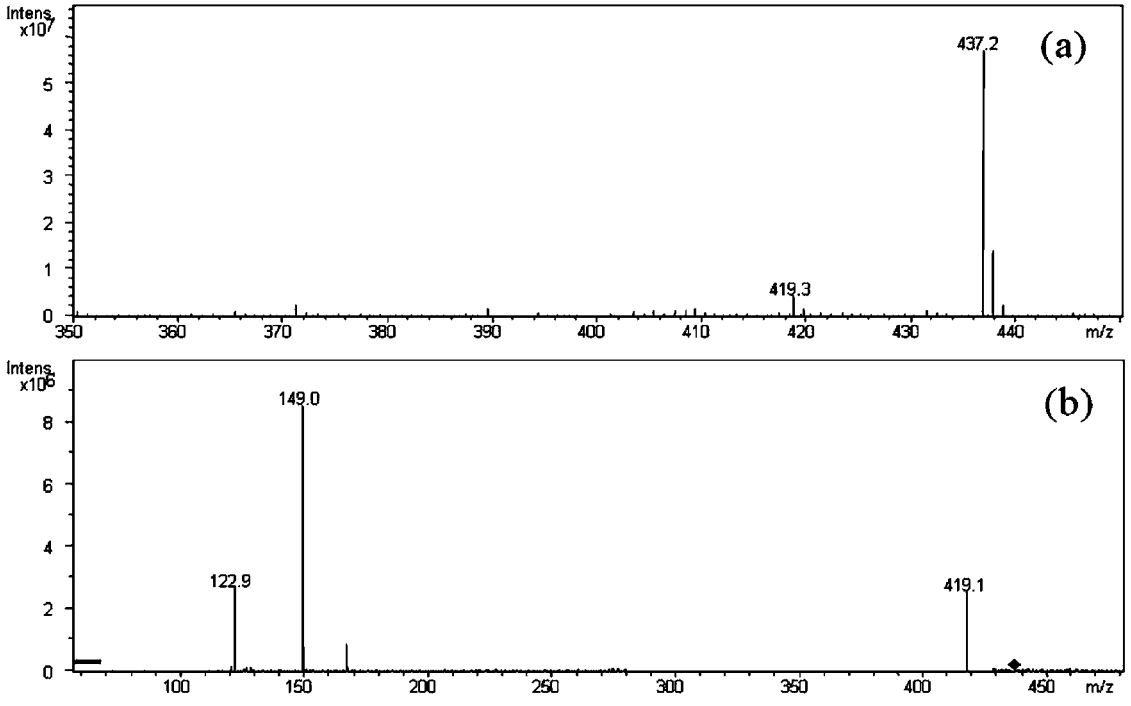

Figure 4. Identification of dimethylarsinoyl fatty acid present in BCR-279: (a) mass spectrum of dimethylarsinoyl fatty acid; (b) MS/MS spectrum of *m/z* 437.

dentata. As(III), As(V), MMA, DMA, and AsB were detected in several seaweeds analyzed. Furthermore, as shown in Figure S2 (Supporting Information), $ArCl^+$ was detected in the extract of *Undaria pinnatifida* due to the high chloride content in the sample. It was well separated from MMA and As(V) and did not cause any interferences. In this study the peak areas of the elution peaks were used for quantifications. The recoveries listed in Tables 2 and 3 are determined by spiking the seaweed

dx.doi.org/10.1021/jf204595d | J. Agric. Food Chem. 2012, 60, 2083−2089

samples with known amounts of the arsenic species studied and then extracting by a of mixture methanol and mobile phase A solution as described above. As shown, recoveries were in the range of 90−106% for the species studied in different samples. The amounts of arsenic present in these seaweed samples were quantified by an external calibration method, and the results are listed in Tables 2 and 3. The major arsenic species present varied with the type of seaweed. Because the calibration sensitivities of various arsenic species based on peak area were similar, the concentrations of the compounds for which standards are not available were estimated against the sensitivity of the nearest peak. As shown, the IC-ICP-MS results were compared with the total concentrations of arsenic in these seaweed samples quantified after complete dissolution of samples and found to be in satisfactory agreement with the total concentrations. The precision between sample replicates, of different experiments including extraction, separation, and determination (n = 3), was >9% for all determinations.

■ ASSOCIATED CONTENT

Supporting Information

Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sjjiang@faculty.nsysu.edu.tw. Fax: 886-7-5253908.

Funding

This research was supported by a grant from the National Science Council of the Republic of China under contract NSC 97-2113-M-110-008-MY3.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Pizarro, I.; Gómez, M.; Cámara, C.; Palacios, M. A. Arsenic speciation in environmental and biological samples: extraction and stability studies. *Anal. Chim. Acta* **2003**, *495*, 85−98.

(2) Cao, X.; Hao, C. L.; Wang, G.; Yang, H. H.; Chen, D. Y.; Wang, X. R. Sequential extraction combined with HPLC-ICP-MS for As speciation in dry seafood products. *Food Chem.* **2009**, *113*, 720−726.

(3) Le, X.-C.; Lu, X.; Li, X.-F. Arsenic speciation. *Anal. Chem.* **2004**, *76*, 27A−33A.

(4) McSheehy, S.; Szpunar, J.; Morabito, R.; Quevauviller, P. The speciation of arsenic in biological tissues and the certification of reference materials for quality control. *Trends Anal. Chem.* **2003**, *22*, 191−209.

(5) Guerin, T.; Leufroy, A.; Noel, L.; Dufailly, V.; Beauchemin, D. Determination of seven arsenic species in seafood by ion exchange chromatography coupled to inductively coupled plasma-mass spectrometry following microwave assisted extraction: method validation and occurrence data. *Talanta* **2011**, *83*, 770−779.

(6) Wang, R.-Y.; Hsu, Y.-L.; Chang, L.-F.; Jiang, S.-J. Speciation analysis of arsenic and selenium compounds in environmental and biological samples by ion chromatography-ICP-DRC-MS. *Anal. Chim. Acta* **2007**, *590*, 239−244.

(7) Jedynak, L.; Kowalska, J.; Harasimowicz, J.; Golimowski, J. Speciation analysis of arsenic in terrestrial plants from arsenic contaminated area. *Sci. Total Environ.* **2009**, *407*, 945−952.

(8) Bednar, A. J.; Garbarino, J. R.; Burkhardt, M. R.; Ranville, J. F.; Wildeman, T. R. Field and laboratory arsenic speciation methods and their application to natural-water analysis. *Water Res.* **2004**, *38*, 355−364.

(9) Slejkovec, Z.; Falnoga, I.; Goessler, W.; van Elteren, J. T.; Raml, R.; Podgornik, H.; Cernelc, P. Analytical artefacts in the speciation of arsenic in clinical samples. *Anal. Chim. Acta* **2008**, *607*, 83−91.

(10) Chen, L. W. L.; Lu, X.; Le, X. C. C. Complementary chromatography separation combined with hydride generation−inductively coupled plasma mass spectrometry for arsenic speciation in human urine. *Anal. Chim. Acta* **2010**, *675*, 71−75.

(11) Tian, Y.; Chen, M.-L.; Chen, X.-W.; Wang, J.-H.; Hirano, Y.; Sakamoto, H.; Setsu, I. Arsenic speciation with gradient hydride generation interfacing liquid chromatography and atomic absorption spectrometry. *J. Anal. At. Spectrom.* **2010**, *25*, 48−54.

(12) Rabieh, S.; Hirner, A. V.; Matschullat, J. Determination of arsenic species in human urine using high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS). *J. Anal. At. Spectrom.* **2008**, *23*, 544−549.

(13) Kannamkumarath, S. S.; Wrobel, K.; Caruso, J. A. Speciation of arsenic in different types of nuts by ion chromatography-inductively coupled plasma mass spectrometry. *J. Agric. Food Chem.* **2004**, *52*, 1458−1463.

(14) Raber, G.; Francesconi, K. A.; Irgolic, K. J.; Goessler, W. Determination of 'arsenosugars' in algae with anion-exchange chromatography and an inductively coupled plasma mass spectrometer as element-specific detector. *Fresenius' J. Anal. Chem.* **2000**, *367*, 181−188.

(15) Wang, M.; Feng, W.; Shi, J.; Zhang, F.; Wang, B.; Zhu, M.; Li, B.; Zhao, Y.; Chai, Z. Development of a mild mercaptoethanol extraction method for determination of mercury species in biological samples by HPLC-ICP-MS. *Talanta* **2007**, *71*, 2034−2039.

(16) Donard, O. F. X.; Lalere, B.; Martin, F.; Lobinski, R. Microwave-assisted leaching of organotin compounds from sediments for speciation analysis. *Anal. Chem.* **1995**, *67*, 4250−4254.

(17) Tseng, C. M.; De Diego, A.; Martin, F. M.; Donard, O. F. X. Rapid and quantitative microwave-assisted recovery of methylmercury from standard reference sediments. *J. Anal. At. Spectrom.* **1997**, *12*, 629−635.

(18) Yeh, C.-F.; Jiang, S.-J. Speciation of arsenic compounds in fish and oyster tissues by capillary electrophoresis ICP-MS. *Electrophoresis* **2005**, *26*, 1615−1621.

(19) Van Hulle, M.; Zhang, C.; Zhang, X.; Cornelis, R. Arsenic speciation in Chinese seaweeds using HPLC-ICP-MS and HPLC-ES-MS. *Analyst* **2002**, *127*, 634−640.

(20) Corr, J. J.; Larsen, E. H. Arsenic speciation by liquid chromatography coupled with ionspray tandem mass spectrometry. *J. Anal. At. Spectrom.* **1996**, *11*, 1215−1224.

(21) Gallagher, P. A.; Wei, X.; Brockhoff, C. A.; Creed, J. T. Detection of arsenosugars from kelp extracts *via* IC-electrospray ionization-MS-MS and IC membrane hydride generation ICP-MS. *J. Anal. Atom. Spectrom.* **1999**, *14*, 1829−1834.

(22) McSheehy, S.; Marcinek, M.; Chassaigne, H.; Szpunar, J. Identification of dimethylarsinoyl-riboside derivatives in seaweed by pneumatically assisted electrospray tandem mass spectrometry. *Anal. Chim. Acta* **2000**, *410*, 71−84.

(23) Madsen, A. D.; Goessler, W.; Pedersen, S. N.; Francesconi, K. A. Characterization of an algal extract by HPLC-ICP-MS and LC-electrospray MS for use in arsenosugar speciation studies. *J. Anal. At. Spectrom.* **2000**, *15*, 657−662.

(24) Chu, Y.-L.; Jiang, S.-J. Speciation analysis of arsenic compounds in edible oil by ion chromatography−inductively coupled plasma mass spectrometry. *J. Chromatogr., A* **2011**, *1218*, 5175−5179.

(25) Brisbin, J. A.; B'Hymer, C.; Caruso, J. A. A gradient anion exchange chromatographic method for the speciation of arsenic in lobster tissue extracts. *Talanta* **2002**, *58*, 133−145.

(26) Vela, N. P.; Heitkemper, D. T.; Stewart, K. R. Arsenic extraction and speciation in carrots using accelerated solvent extraction, liquid chromatography and plasma mass spectrometry. *Analyst* **2001**, *126*, 1011−1017.

(27) Foster, S.; Maher, W.; Krikowa, F.; Apte, S. A microwave-assisted sequential extraction of water and dilute acid soluble arsenic

species from marine plant and animal tissues. *Talanta* **2007**, *71*, 537−549.

(28) Feldmann, J.; Amayo, K. O.; Petursdottir, A.; Newcombe, C.; Gunnlaugsdottir, H.; Raab, A.; Krupp, E. M. Identification and quantification of arsenolipids using reversed-phase HPLC coupled simultaneously to high-resolution ICPMS and high-resolution electrospray MS without species-specific standards. *Anal. Chem.* **2011**, *83*, 3589−3595.

(29) Mattusch, J.; Arroyo-Abad, U.; Mothes, S.; Moeder, M.; Wennrich, R.; Elizalde-Gonzalez, M. P.; Matysik, F. M. Detection of arsenic-containing hydrocarbons in canned cod liver tissue. *Talanta* **2010**, *82*, 38−43.