



## A survey of arsenic species in chinese seafood

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### Abstract

In the present report, thirty different types of Chinese edible seafood, including brown algae, red algae, fish, crab, shrimp, mussels, oysters, and clams, which are very popular foodstuffs in the Chinese kitchen, were examined for their total content of As as well as its different species. Total arsenic concentration in algae samples was 1.7–38.7 µg/g (dry weight), and 0.086–7.54 µg/g in fish and shellfish (wet weight), respectively. The arsenic species in seafood extracts were determined by using anion and cation exchange high performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICPMS). Arseno-sugars were detected in all of the extracted algae samples (1.5–33.8 µg/g dry weight) and fish samples (0.018–0.78 µg/g wet weight). Arsenobetaine was detected in all of the extracted fish and shellfish samples (0.025–6.604 µg/g wet weight). In contrast, inorganic arsenic in fish and shellfish samples occurred at levels below 2% of the total arsenic. No inorganic arsenic was detected in the algae samples. This study provides information about the distribution pattern of arsenic species in seafood products. Since the major share of arsenic components in seafood is organic arsenic with a low toxicity, we can conclude that arsenic in seafood does not pose any risk to human health.

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### 1. Introduction

Arsenic has a century-long reputation of being poisonous (Polson and Tattersall, 1969; Nriagu, 1994). However, the toxicity of arsenic is greatly dependent on its chemical form (Penrose, 1974; Andreae, 1986; Kaise and Fukui, 1992). For example, the 50% lethal dose (LD<sub>50</sub>) values in rats for some arsenic species are (in mg/kg): arsine 3, arsenite 14, arsenate 20, monomethylarsonic acid 700–1800, dimethylarsinic acid 700–2600, arsenobetaine > 10,000, and arsenocholine 6500 (Nriagu, 1994).

Seafood (algae, fish, and shellfish) is very popular in the Chinese cuisine. In China, large amounts of seafood are now cultivated and harvested. It is the focus of a billion-dollar aquaculture industry. Arsenic is present in high concentrations (orders of micrograms per gram) in seafood. However, there is no species defined legislative

control in most countries (Buchet et al., 1994; Francesconi and Edmonds, 1994; Phillips, 1994). The limit for arsenic in drinking water in China is 50 µg/l. This is largely based on inorganic arsenite and arsenate. If this limit was applied to seafood, most of it would be unfit for consumption, given the fact that arsenic content in seafood exceeds that in drinking water by a factor of 1000 (National Academy of Sciences, 1997; Cullen and Reimer, 1989). Along with seafood dietary intake, questions concerning possible toxic aspects of these types of seafood arise. Traditional approaches based on the determination of total element concentrations are no longer sufficient to assess the health risks involving arsenic exposure and intake. This paper gives a survey of the total content and the chemical speciation of arsenic in 30 popular Chinese types of seafood, originating from different sea areas. Therefore, it is very important to accurately estimate the different forms of arsenic present as well as the total concentration in seafood (Velez et al., 1996).

Total arsenic concentrations in seafood was determined using microwave assisted digestion (Feldmann et

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al., 2000) and inductively coupled plasma mass spectrometry (ICPMS). The arsenic species in seafood extracts were examined using anion exchange and cation exchange high performance liquid chromatography in combination with ICPMS.

## 2. Materials and methods

### 2.1. Reagents

All reagents were of analytical grade unless otherwise mentioned. Pyridine was from Shanghai Chemical Reagent Co. (Shanghai, China).  $\text{NH}_4\text{HCO}_3$  was from Beijing Chemical Reagent Co. (Beijing, China). Methanol was purchased from Tianjin Si You Biochemical Co. (Beijing, China).  $\text{HNO}_3$  was purchased from Beijing Shiji (Beijing, PR China). 18M $\Omega$  deionized water (Beijing Shuangfeng pure water equipment factory) was used throughout the whole experiment. Arsenate stock solutions were prepared from  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma, St. Louis, MO, USA). Arsenobetaine (AsB), arsenocholine (AsC) and dimethylarsinic acid (DMA) were provided by the Commission of the European Communities, Standard, Measurement and Testing Programme. Arsenosugar  $\text{PO}_4$  and OH were isolated from natural sources with the method developed by the present authors, which will be published in another article. The kelp powder was donated by Dr. S.A. Pergantis (Birkbeck College, University of London, UK). The four arsenosugars 3-[5'-deoxy-5'(dimethylarsinoyl)- $\beta$ -ribofuranosyloxy]-2-hydroxypropylene glycol (arsenosugar OH), 3-[5'-deoxy-5'(dimethylarsinoyl)- $\beta$ -ribofuranosyloxy]-2-hydroxypropyl 2,3-hydroxypropyl-phosphate (arsenosugar  $\text{PO}_4$ ), 3-[5'-deoxy-5'(dimethylarsinoyl)- $\beta$ -ribofuranosyloxy]-2-hydroxypropanesulfonic acid (arsenosugar  $\text{SO}_3$ ) and 3-[5'-deoxy-5'(dimethylarsinoyl)- $\beta$ -ribofuranosyloxy]-2-hydroxypropyl hydrogensulphate (arsenosugar  $\text{SO}_4$ ) initially used to characterize the arsenic species in the kelp extract were a kind gift of Dr. K.A. Francesconi (Karl-Franzens University, Graz,

Austria). The different arsenic species are listed in Table 1.

### 2.2. Instrumentation

The HPLC system consisted of an Alltech Model 526 metal free pump (Deerfield, IL, USA), a Model 9010 metal-free switching valve with sample loop volumes of 50  $\mu\text{L}$  (Rheodyne, Cotata, CA, USA), an Ionpac CS10 cation exchange column (Dionex, Sunnyvale, CA, USA) and a PRP-X100 anion exchange column (Hamilton, Reno, NV, USA). An Elan 6000 ICP-MS (PE Sciex, Toronto, Canada) was used throughout this study. Operating conditions of the ICP-MS and the chromatographic conditions are listed in Table 2.

### 2.3. Sample collection

Following the reply about their dietary habits of a random sample of 50 habitants in Beijing China, we selected 30 types of seafood, which are commonly used in the Chinese kitchen. The seafood samples were collected during April 2002 from large supermarkets in Beijing. A description of the samples, and the place of origin of the raw seafood are shown in Table 3.

### 2.4. Procedures

#### 2.4.1. Sample extraction

Dried seaweed (0.5 g dry weight), and meat of fresh fish or shellfish (5 g wet weight) were grinded in a stainless steel grinding mill. Afterwards the samples were placed in a centrifuge tube to which a 10 ml 1:1 v/v methanol/water mixture was added. The tubes were sonicated and centrifuged for 10 min. The extract was removed and placed in round bottom flasks. The extraction procedure was repeated another four times. The combined extracts were rotary evaporated at 30  $^\circ\text{C}$  to dryness and dissolved in 10 ml of deionized water. The extracts were stored at 4  $^\circ\text{C}$  prior to analysis.

Table 1  
Formulae of some arsenic compounds

Arsenic compound	Formula
Arsenite ( $\text{As}^{3+}$ )	$\text{As}(\text{OH})_3$
Arsenate ( $\text{As}^{5+}$ )	$\text{AsO}(\text{OH})_3$
Monomethylarsonic acid (MMA)	$\text{CH}_3\text{AsO}(\text{OH})_2$
Dimethylarsinic acid (DMA)	$(\text{CH}_3)_2\text{AsO}(\text{OH})$
Arsenobetaine (AsB)	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COOH}$
Arsenocholine (AsC)	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$
Arsenosugar $\text{PO}_4$	$\text{R} = \text{OP}(\text{O})(\text{OH})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$
Arsenosugar OH	$\text{R} = \text{OH}$
Arsenosugar $\text{SO}_3$	$\text{R} = \text{SO}_3\text{H}$
Arsenosugar $\text{SO}_4$	$\text{R} = \text{OSO}_3\text{H}$

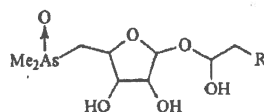


Table 2  
Operating conditions of the ICPMS and the chromatographic systems

Inductively coupled plasma mass spectrometry (ICPMS)	
Radio frequency power	1200 W
Sampler and skimmer cones	Nickel
Spray chamber	Double-pass (Scott type)
<i>Argon flow rates:</i>	
Plasma/coolant	15 l/min
Auxiliary	0.8 l/min
Nebulizer	0.96 l/min
Date acquisition mode	Graphics (signal intensity versus time)
Chromatography	
<i>Cation exchange</i>	
Guard column	Dionex Ionpac CS-10 (50×4 mm id, 10 μm)
Analytical column	Dionex Ionpac CS-10 (250×4 mm id, 10 μm)
Mobile phase	5 mmol l <sup>-1</sup> pyridinium adjusted to pH 2.0 with HNO <sub>3</sub>
<i>Anion exchange</i>	
Guard column	Hamilton PRP-X100 (25×2.3 mm id, 12–20 μm)
Analytical column	Hamilton PRP-X100 (250×4.1 mm id, 10 μm)
Mobile phase	20 mmol l <sup>-1</sup> NH <sub>4</sub> HCO <sub>3</sub> adjusted to pH 10.3 with NH <sub>4</sub> OH
Flow rate	1.0 ml min <sup>-1</sup>
Injection volume	50 μl

#### 2.4.2. Sample digestion

0.1 g of dried algae, 3 ml of HNO<sub>3</sub> and 2 ml H<sub>2</sub>O<sub>2</sub> were added into a PTFE bomb. After 10 min the bombs were sealed off and put in a microwave oven at a power of 315 W for 5 min. Afterwards the vessel was cooled down. The clear solution was diluted to 10 ml using deionized water, diluted 1:9 and filtered prior to analysis.

To fish and shellfish tissues, 1 g of each of the samples were added to the bomb containing 5 ml HNO<sub>3</sub> and 2 ml H<sub>2</sub>O<sub>2</sub>. After 15 min the closed bombs were placed in the microwave oven, using the following program: 5 min at 63 W, 5 min at 155 W, 10 min at 315 W and 5 min at 470 W. After each step the vessels were cooled down and gas was released. The clear solution was diluted to 10 ml using deionized water (Feldmann et al., 2000).

#### 2.4.3. Total arsenic analysis

Total arsenic content in the seafood samples was measured before and after extraction using inductively coupled plasma mass spectrometry. <sup>187</sup>Re was used as an internal standard. 1 ml of the digested sample was diluted with 9 ml 1% HNO<sub>3</sub>.

The accuracy of the measurement was tested by the analysis of a certified reference material, BCR-CRM 627 (tuna fish sample, Institute for Reference Materials and Measurement, Belgium), which had a certified value of 4.8±0.3 mg kg<sup>-1</sup> As. The value we obtained was 5.0±0.3 mg kg<sup>-1</sup>. A recovery test was also carried out in the present study. The recovery values by spiking 20 ng ml<sup>-1</sup> of As<sup>3+</sup>, As<sup>5+</sup>, MMA and DMA are 96%, 101%, 95%, 100%, respectively (expressed as the mean of three independent analyses).

#### 2.4.4. Arsenic speciation

The arsenic species in seafood extracts were examined using anion exchange and cation exchange high performance liquid chromatography in combination with ICPMS.

Anion exchange and cation exchange chromatography conditions are shown in Table 2. The arsenic compounds in the extracts were identified by matching their retention times with those of standards. Identification of arsenosugars in the extracts was done by comparing the retention times with those present in kelp powder. Kelp powder contains four arsenosugars. An extract of kelp powder was analyzed by HPLC-ICPMS and the arsenic compounds were identified by using electrospray mass spectrometry (Van Hulle et al., 2002). It should be noted that the concentrations of arsenic species reported in Tables 4 and 5 were based on calibration curves prepared from arsenate. Measurements by ICPMS are, however, not supposed to be influenced by the type of arsenic compound.

### 3. Results and discussion

#### 3.1. Total arsenic concentration

Table 3 summarizes the total amount of arsenic and shows the extractability of arsenic in the different samples. Consistent with earlier studies, total arsenic concentrations (dry weight) were highest in algae (values range from 1.7 μg/g in red algae to 38.7 μg/g in brown algae). Values of arsenic in fish and shellfish range from 0.086 μg/g to 7.54 μg/g (concentrations reported as elemental arsenic

Table 3  
Total arsenic concentration in the samples (algae samples: mg/kg dry weight; fish and shellfish samples: mg/kg wet weight)

Sample	Source	Total arsenic <sup>a</sup>	Extraction efficiency (%)
<b>Fish</b>			
Needlefish 1	Bo sea	0.86±0.03	86
Needlefish 2	Bo sea	0.57±0.03	83
Yellowfin Tuna	Bo sea	2.38±0.08	73
Flatfish	Yellow sea	0.32±0.01	83
Hairtail	Yellow sea	0.75±0.03	70
Red fish	Yellow sea	0.26±0.01	69
Hake	East sea	0.83±0.02	76
Sardine	East sea	0.64±0.03	61
<b>Shellfish</b>			
<i>Squid</i>			
Squid 1	Bo sea	0.24±0.02	90
Squid 2	Bo sea	0.37±0.02	89
<i>Crustaceans</i>			
Crab1	East sea	7.54±0.06	89
Crab2	Bo sea	0.76±0.02	91
Crab3	East sea	0.96±0.04	83
Shrimp1	Yellow sea	0.45±0.02	88
Shrimp2	East sea	2.18±0.06	83
<i>Bivalves</i>			
Oyster	Bo sea	0.09±0.07	78
Clam	East sea	2.13±0.07	80
Mussel 1	East sea	0.57±0.03	84
Mussel 2	Bo sea	0.22±0.02	81
Mussel 3	Bo sea	0.72±0.03	80
<b>Algae</b>			
Red algae 1	Bo sea	7.9±0.3	93
Red algae 2	Yellow sea	1.7±0.2	96
Red algae 3	East sea	19.3±0.4	93
Red algae 4	South sea	1.7±0.1	90
Red algae 5	Bo sea	3.4±0.2	92
Brown algae 1	South sea	38.7±0.6	87
Brown algae 2	Bo sea	23.8±0.4	90
Brown algae 3	Bo sea	31.4±0.3	93
Brown algae 4	East sea	28.1±0.6	91
Brown algae 5	East sea	14.6±0.2	90

<sup>a</sup> The precision is expressed as ± one standard deviation.

per tissue weight). Marked variation in total arsenic concentrations observed in seafood samples reflects the variation among species.

The results indicated in Table 3 show that the extraction efficiency was high (>80%) in most seafood samples. This is due to the methanol/water extraction method, widely used to extract arsenic species from seafood with a very good efficiency (Lai et al., 1997). However, the extraction efficiency was lower (<70%) for sardine, redfish and hairtail. The lower extraction efficiencies in these samples could be attributed to the presence of fatty substances. Hydrophobic compounds might reduce the efficiency of methanol/water extractant by forming a film that prevents moisture uptake by the sample. Moreover there could be arsenolipids present in these products, which are not extractable with methanol/water.

### 3.2. Speciation of arsenic with HPLC-ICPMS

Anion exchange chromatography was used for the separation of nine arsenic species (AsB, As<sup>3+</sup>, MMA, As<sup>5+</sup>, DMA, and the four arsenosugars). The resulting chromatograms of the compounds are shown in Figs. 1 and 2. Using anion exchange AsB and arsenosugar OH have the same retention time of 170 s. In order to resolve this problem, cation exchange chromatography was used. The separation of arsenosugar OH and PO<sub>4</sub>, AsB, AsC and DMA was successfully achieved using a 5 mmol l<sup>-1</sup> pyridinium formate mobile phase. The resulting chromatogram is shown in Fig. 3.

“Zicai” and “Haidai” are two popular algae in China. Both contain arsenosugars as the major arsenic species (Le et al., 1994; Madsen et al., 2000). Zicai is a kind of red algae. Extracts of both algae were analyzed with anion exchange chromatography and cation exchange chromatography as shown in Fig. 4a and b. The arsenic content is exclusively due to the presence of arsenosugar OH and arsenosugar PO<sub>4</sub> in all red algae samples. The concentration of arsenosugars in Zicai from different sea areas varies (1.5 µg/g in the South sea and 17.9 µg/g

Table 4  
Concentrations of arsenic compounds in extracts of algae (As mg/kg dry weight)

Sample	Total extractable arsenic	Arsenosugar PO <sub>4</sub>	Arsenosugar OH	Arsenosugar SO <sub>3</sub>	DMA
Red algae 1	7.4±0.4	4.7±0.3	2.7±0.2	L.O.D.**	L.O.D.
Red algae 2	1.6±0.2	0.4±0.1	1.2±0.2	L.O.D.	L.O.D.
Red algae 3	17.9±1.2	12.7±0.9	5.2±0.4	L.O.D.	L.O.D.
Red algae 4	1.5±0.5	0.2±0.1	1.3±0.4	L.O.D.	L.O.D.
Red algae 5	3.1±0.6	2.1±0.4	1.0±0.2	L.O.D.	L.O.D.
Brown algae 1	33.8±2.2	7.1±0.5	7.1±0.5	17.6±1.2	2.0±0.2
Brown algae 2	21.5±1.8	1.4±0.1	6.3±0.5	10.6±1.1	3.2±0.2
Brown algae 3	29.3±1.9	3.5±0.3	7.8±0.5	12.9±1.2	5.1±0.4
Brown algae 4	29.6±0.9	5.1±0.2	6.8±0.3	15.4±0.5	2.3±0.1
Brown algae 5	13.1±1.1	0.9±0.1	1.6±0.2	8.9±1.0	1.7±0.2

L.O.D.\*\*: limit of detection.

Table 5  
concentrations of arsenic compounds in extracts of fish and shellfish (As mg/kg wet weight)

Samples	Total extractable arsenic	DMA	AsB	Arsenosugar PO <sub>4</sub>	Arsenosugar OH	U	Inorg. arsenic
<b>Fish</b>							
Needlefish 1	0.74±0.02	L.O.D.*	0.73±0.02	L.O.D.	L.O.D.	L.O.D.	0.011±0.002
Needlefish 2	0.48±0.02	L.O.D.	0.47±0.02	L.O.D.	L.O.D.	L.O.D.	0.007±0.001
Yellowfin Tuna	1.74±0.07	L.O.D.	1.73±0.07	L.O.D.	L.O.D.	L.O.D.	0.014±0.002
Flatfish	0.27±0.01	L.O.D.	0.26±0.01	L.O.D.	L.O.D.	L.O.D.	0.003±0.001
Hartail	0.53±0.03	L.O.D.	0.52±0.03	L.O.D.	L.O.D.	L.O.D.	0.009±0.001
Red fish	0.18±0.01	0.045±0.003	0.13±0.01	L.O.D.	L.O.D.	L.O.D.	0.003±0.001
Hake	0.63±0.02	L.O.D.	0.62±0.02	L.O.D.	L.O.D.	L.O.D.	0.007±0.001
Sardine	0.39±0.02	L.O.D.	0.38±0.02	L.O.D.	L.O.D.	L.O.D.	0.006±0.001
<b>Shellfish</b>							
<i>Squid</i>							
Squid 1	0.21±0.01	L.O.D.	0.15±0.02	0.06±0.01	L.O.D.	L.O.D.	0.002±0.001
Squid 2	0.33±0.02	L.O.D.	0.24±0.02	0.08±0.01	L.O.D.	L.O.D.	0.003±0.001
<i>Crustaceans</i>							
Crab 1	6.68±0.05	L.O.D.	6.60±0.05	L.O.D.	L.O.D.	L.O.D.	0.073±0.005
Crab 2	0.69±0.02	L.O.D.	0.68±0.02	L.O.D.	L.O.D.	L.O.D.	0.005±0.001
Crab 3	0.80±0.05	L.O.D.	0.79±0.05	L.O.D.	L.O.D.	L.O.D.	0.005±0.001
Shrimp1	0.39±0.02	0.029±0.002	0.34±0.02	0.02±0.01	L.O.D.	L.O.D.	0.002±0.001
Shrimp2	1.81±0.06	L.O.D.	1.22±0.04	0.59±0.03	L.O.D.	L.O.D.	0.006±0.001
<i>Bivalves</i>							
Oyster	0.07±0.01	0.004±0.001	0.03±0.01	0.04±0.01	0.001±0.001	L.O.D.	L.O.D.
Clam	1.70±0.05	L.O.D.	0.79±0.03	0.75±0.03	0.027±0.002	0.11±0.01	0.014±0.002
Mussel 1	0.43±0.03	L.O.D.	0.27±0.02	0.14±0.01	0.014±0.001	L.O.D.	0.004±0.001
Mussel 2	0.18±0.01	L.O.D.	0.11±0.01	0.07±0.01	0.006±0.001	L.O.D.	0.003±0.001
Mussel 3	0.58±0.03	L.O.D.	0.48±0.03	0.08±0.01	0.016±0.001	L.O.D.	0.003±0.001

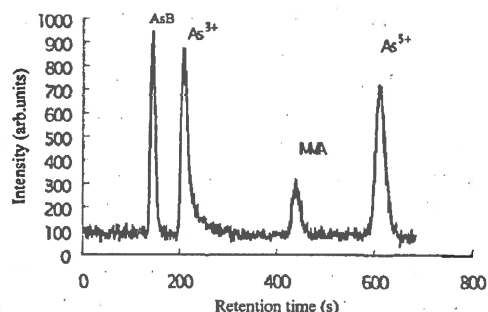


Fig. 1. Anion exchange HPLC-ICPMS chromatogram of four different arsenic standards: AsB, As<sup>3+</sup>, MMA, and As<sup>5+</sup>; for conditions see Table 2.

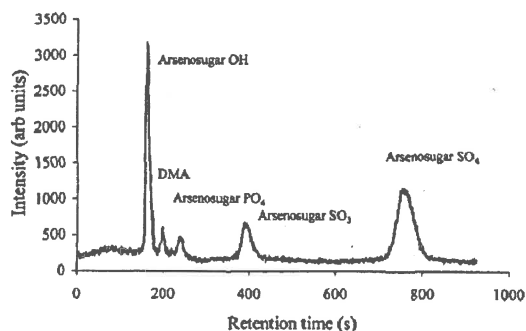


Fig. 2. Anion exchange HPLC-ICPMS chromatogram of an extract of kelp powder; for conditions see Table 2.

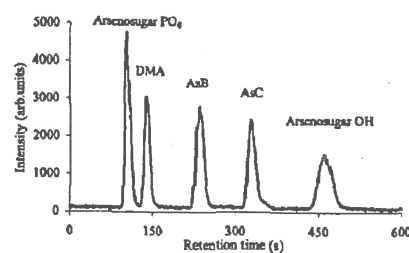


Fig. 3. Cation exchange HPLC-ICPMS chromatogram of five different arsenic standards: AsB, AsC, DMA, arsenosugar OH and arsenosugar PO<sub>4</sub>; for conditions see Table 2.

in the East sea). In algae samples originating from different sea areas, the share of the arsenosugar PO<sub>4</sub> (13.3–67.7%) and arsenosugar OH (19.1–86.2%) in total arsenic also varies.

“Haidai” is a kind of brown algae. The anion exchange HPLC-ICPMS analyses show that arsenosugar OH, arsenosugar PO<sub>4</sub>, arsenosugar SO<sub>3</sub> and DMA were identified in all of the Haidai samples (Fig. 5). The highest arsenosugar concentration was found in the Haidai (13.1–33.8 µg/g dry weight). For this algae, the arsenosugar content reported by other authors (Harrington et al., 1997) are in the range of 13.4–44.5 µg/g (dry weight). DMA content in this alga amounts to 1.7–5.1 µg/g (dry weight).

AsB was detected in all of the fish and shellfish samples analyzed. The highest AsB concentration was

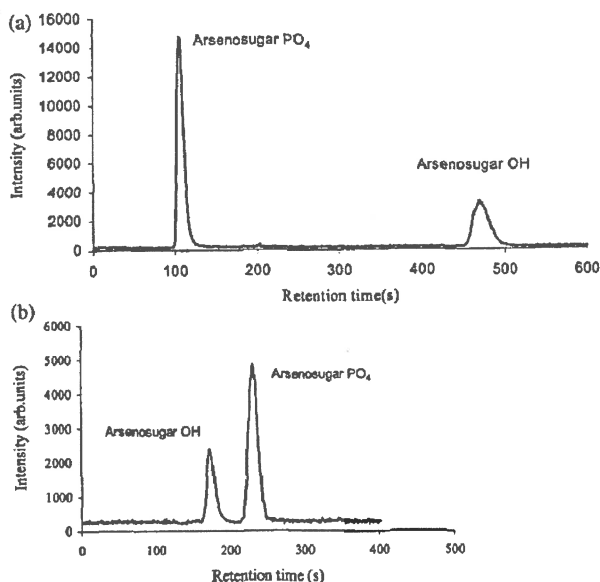


Fig. 4. (a) Cation exchange HPLC-ICPMS chromatogram of an extract of red algae (sample 5); for conditions see Table 2; (b) anion exchange HPLC-ICPMS chromatogram of an extract of red algae (sample 5); for conditions see Table 2.

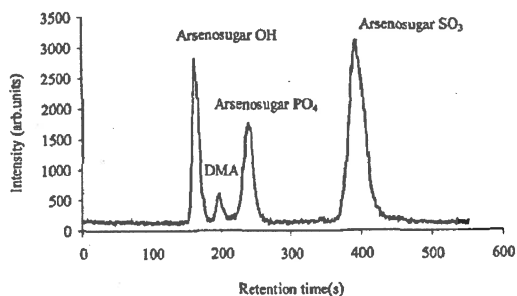


Fig. 5. Anion exchange HPLC-ICPMS chromatogram of an extract of Haidai (Bo Sea); for conditions see Table 2.

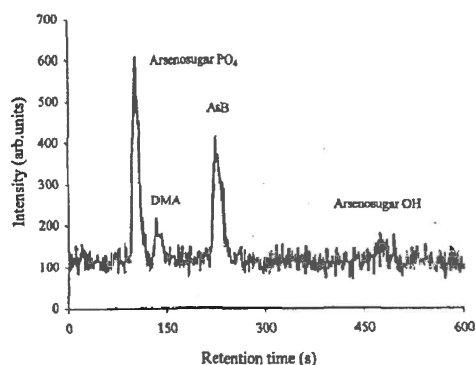


Fig. 6. Cation exchange HPLC-ICPMS chromatogram of an extract of oyster; for conditions see Table 2.

found in a sample of crab: 6.60  $\mu\text{g/g}$  (wet weight), followed by yellowfin-tuna: 1.73  $\mu\text{g/g}$  (wet weight). For the remaining samples of fish analyzed, the concentrations were relatively homogeneous. In all fish samples (except redfish), arsenobetaine was the species that represented the highest percentage of total extractable arsenic (exceeding 98%). Arsenobetaine is a relatively stable compound and innocuous to humans (Cannon et al., 1981). Several groups have reported that arsenobetaine is directly excreted from the human body not being metabolized (Francesconi and Edmonds, 1997).

Arsenosugar  $\text{PO}_4$  is also detected in all the shrimp and bivalves samples analyzed in this study. It is particularly interesting to note the presence of the arsenosugar  $\text{PO}_4$  and the relatively high concentration of arsenic in a shrimp (588 ng/g wet weight). It has been claimed by some researchers that arsenocholine is present in shrimp, but others could not confirm its presence (Cullen and Reimer, 1989). We have not found evidence for the presence of arsenocholine in shrimp in the present study.

In the shellfish group each of the products studied had a different pattern of composition. In bivalves (mussel, clam, and oyster) there was a predominance of arsenosugar  $\text{PO}_4$  (14.4–55.2%) and arsenobetaine (37.3–82.3%), although the percentage of arsenobetaine was far below the values for fish. Arsenosugar OH appeared in all bivalves sample, although it did not exceed 5.7% (1.5–5.7%). The arsenosugar  $\text{PO}_4$  and arsenosugar OH along with arsenobetaine are found to be the major arsenic species in oyster (Fig. 6) and clam. These results are in agreement with those found in a previous report (Le et al., 1994). This confirms that bivalves contain not only arsenobetaine but also arsenosugars as the major arsenic compound. Although Shibata et al. suggested that arsenosugars have no cytotoxicity or mutagenicity (Shibata et al., 1990), they are metabolized to arsenic species as DMA in the body after ingestion of algae. DMA is more toxic than arsenosugars (Yamamoto et al., 1994). DMA did not appear in all of the samples analyzed, whereas was detected only in the redfish (45 ng/g wet weight) (Fig. 7), representing 25.1% of the

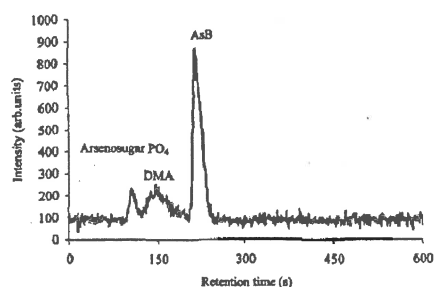


Fig. 7. Cation exchange HPLC-ICPMS chromatogram of an extract of redfish; for conditions see Table 2.

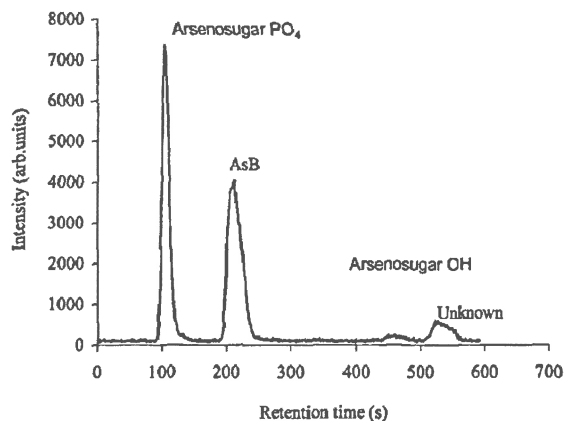


Fig. 8. Cation exchange HPLC-ICPMS chromatogram of an extract of clam; for conditions see Table 2.

total arsenic. It was also detected in a sample of shrimp (29 ng/g wet weight) and oyster (4 ng/g wet weight).

An unknown arsenic species was found in a sample of clam (Fig. 8) representing 6.5% of the total arsenic. This species of arsenic did not appear in other samples analyzed.

The seafood samples in this study originated from diverse geographic location (Table 3). This diversity reflects the homogeneous nature of contemporary China seafood supplies. Consequently, the arsenic concentrations from this survey are likely to be generally representative of typical concentrations in seafood throughout China.

The distribution profile of arsenic species (AsB, DMA, and four arsenosugars) was characterized in seven different seafood items. In all of the algae samples, the predominate species were arsenosugars. In all of the fish and shellfish samples, the predominate species was arsenobetaine. In fish arsenobetaine represents 98% of total extractable arsenic (except redfish). In bivalves, the percentages of arsenic in the form of arsenobetaine was within the ranges of 38.0–62.4%. This could be attributed to the presence of arsenosugars. DMA appeared in only a few seafood samples (shrimp, redfish, oyster and brown algae), in percentages up to 25.1% of the total arsenic (redfish). Little inorganic arsenic (less than 2% of total arsenic) was found in the examined fish and shellfish samples, and no inorganic arsenic was detected in the examined algae.

Since the major arsenic content in seafood is organic with low toxicity, we can conclude that the seafood samples analyzed in this survey are of no risk to human health. However, metabolism of arsenosugars should be taken into consideration when assessing the overall toxicological effect of algae and shellfish consumption.

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