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Inductively coupled plasma mass spectrometry with a continuous-flow dialysis simulated gastrointestinal digestion for study of arsenic bioaccessibility in shrimp

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ABSTRACT

A hyphenated method of continuous-flow dialysis and on-line inductively coupled plasma mass spectrometry (ICP-MS), with and without the use of hydride generation sample introduction, was developed for the study of arsenic bioaccessibility in shrimp. The method was based on a simulated gastric digestion in a batch system followed by a continuous-flow intestinal digestion. The simulated intestinal digestion was performed in a dialysis bag placed inside a channel in a flowing stream of dialyzing solution ($NaHCO_3$). The pH of the dialysate was monitored on-line to ensure pH changes similar to the situation in the gastrointestinal tract. The concentrations of total arsenic and inorganic arsenic in the dialysate were determined by ICP-MS without and with hydride generation, respectively. With the parameters used in the hydride generation as follows: 8% (v/v) of HCl; 1% (m/v) of $NaBH_4$; and a pre-reduction solution (10% (w/v) KI in 5% (w/v) ascorbic acid), only inorganic arsenic can form arsine, implying that hydride generation-ICP-MS can be used to detect inorganic arsenic only. The method was applied for the estimation of arsenic bioaccessibility in shrimp samples, by which the bioaccessibility from shrimp was found to be approximately 55%, contributed from inorganic arsenic only 1% or 2%, and mostly from organic arsenic. Further, the effect of ascorbic acid and fruit juices on arsenic bioaccessibility was investigated which was found not to cause any significant changes in bioaccessibility.

1. Introduction

Seafood is very popular as it is a rich source of proteins, omega-3, fatty acid, vitamin D, iodine, and minerals. However, seafood also contains several metals and metalloids including arsenic [1]. Arsenic has many different forms and the degree of its toxicity depends on its form and oxidation state. Generally, the inorganic forms are more toxic than the organic forms and the trivalent oxidation states are more toxic than the pentavalent oxidation states [2–7]. Arsenic can damage different parts of the body such as skin, lungs, gut, heart, blood vessel, immune system, urinary system, and the nervous system [2]. Arsenic in the human body mostly comes from diet. Therefore, the studies of arsenic forms and bioavailability in food samples are important.

The degree of toxicity of arsenic is dependent on the forms and the oxidation states. Inorganic forms are more toxic than organic forms and the trivalent oxidation states are more toxic than the pentavalent oxidation states [6]. Generally organoarsenic species dominate, but inorganic forms can be found in small quantities in living organisms. Although arsenobetaine is the major species in fish and seafood, minor concentrations of inorganic arsenic, methylated compounds, arsenocholine, or arsenosugars are also found in these marine organisms.

Bioavailability is a term used to describe the proportion of a nutrient in food that can be utilized for normal body function [8]. In human digestive system, digestion and absorption of nutrients are mostly taken place in the stomach and the small intestine. Many techniques [9–14] were proposed for quantification of bioavailability such as *in vivo* method that is the estimation performed in human or animal. Moreover, bioaccessibility, an *in vitro* gastrointestinal simulation method, was used as an approximation for bioavailability [9,11,13–15]. The gastrointestinal simulation is normally carried out under the temperature, pH, and enzyme and chemical conditions which are similar to those found in the human body along the digestive process.

A continuous-flow dialysis system, developed by Shiowatana et al. [16] and applied to many types of food samples [8,16], was applied to study arsenic bioaccessibility in shrimp. It is well known that seafood contains organic arsenic compounds which are of low toxicity compared to their inorganic counterparts. The bioavailability of a particular element can be enhanced or inhibited by the presence of other components in food, the ingredients used in the cooking process, or any other components consumed in the same meal [15–24]. Therefore, it was our interest to examine the effect of ascorbic acid, orange juice, guava juice, apple juice, and grape juice on arsenic bioaccessibility in shrimp. With these aims, inductively

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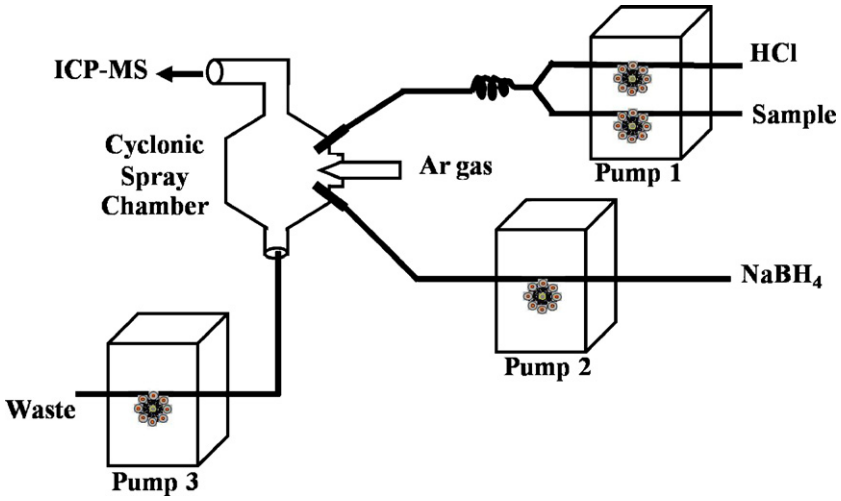

Fig. 1. A schematic diagram showing a set up of hydride generation sample introduction system for ICP-MS detection.

coupled plasma mass spectrometry (ICP-MS) with and without the use of hydride generation sample introduction was utilized as a sensitive element detector for arsenic. Hydride generation was used to provide improved sensitivity and lower detection limit for arsenic determination, and also to separate analytes from sample matrices. Furthermore, under the experimental conditions used in this study, hydride generation-ICP-MS could detect only the inorganic arsenic, whereas ICP-MS could detect both inorganic and organic arsenic. With the two detection approaches, therefore, the inorganic and organic arsenic could be differentiated.

2. Experimental

2.1. Chemicals and samples

Nitric acid (AR 65% assay), hydrochloric acid (AR 37% assay), sodium borohydride (>96%), sodium hydroxide (AR 99% assay), potassium iodide, and ascorbic acid, were purchased from Merck (Darmstadt, Germany). Sodium bicarbonate (AR 99.7–100.3% assay) was from APS Finechem (New South Wales, Australia). Arsenate, arsenite, and arsenobetaine were purchased from Sigma–Aldrich (St. Louis, MO, USA).

A pepsin solution, the digestive enzyme, was prepared by dissolving 0.16 g of pepsin (P-7000, from porcine stomach mucosa, Sigma, USA) in 1 mL of 0.1 mol/L hydrochloric acid. A pancreatin bile extract (PBE) mixture was prepared by dissolving 0.004 g of pancreatin (P-1750, from porcine pancreas, Sigma, USA) and 0.025 g of bile extract (B-6831, porcine, Sigma, USA) in 5 mL of 0.001 mol/L sodium bicarbonate [8].

White shrimp (*Penaeus vanamei*) samples were bought from a local market and were cleaned and rinsed with deionized water. Then, they were dried at 80 °C to constant mass and were stored in a desiccator until use. Fruit juices, i.e., orange, guava, apple, and grape, were bought from a supermarket.

2.2. Instrumentation

A Perkin-Elmer SCIEX model ELAN 6000 ICP-MS instrument (Norwalk, CT, USA) with a glass spray chamber was used for detection of arsenic. The ICP-MS operating conditions for measurement of arsenic are summarized in Table 1. The signal at m/z 75 was used to monitor arsenic. The signals at m/z 77, 82, and 83 were monitored to correct for the isobaric interference from $ArCl^+$.

A schematic diagram of a hydride generation-ICP-MS system is shown in Fig. 1. After pre-reduction of As in the samples, the samples were mixed on-line with the hydrochloric acid solution. Then, they were reacted with the $NaBH_4$ solution in a cyclonic spray chamber to form the gaseous hydrides which were swept with argon gas into the ICP-MS for quantification. Peristaltic pumps (Ismatec, Reglo Analog, Glattbrugg, Switzerland) were used to introduce reagents and sample solutions to the spray chamber that was connected with hydride generation-ICP-MS. The system setup of hydride generation-ICP-MS was similar to that reported by Pohl [25]. The tubing used after the mixing point of HCl and sample to the end of the capillary was 100 cm long with the internal diameter of 0.5 mm. The flow rates used are summarized in Table 1.

The continuous-flow dialysis system used in this study was described elsewhere [8,16]. The outlet of the continuous-flow dialysis system was connected to a pH measurement module and ICP-MS detection unit. An incubator shaker (Memmerts, Memmert GmbH, Germany) was used to shake and incubate samples controlled at 37 ± 1 °C both for simulated gastric and intestinal digestions. The Thermo Orion pH meter model 420 (Beverly, MA, USA) with a glass combination electrode was used for all pH measurements during dialysis process. The dialysis was performed in a dialysis tubing with molecular weight cut-off of 12–14 kDa (Spectra/Por, Thomas Scientific, USA), which was 10 mm wide and 17.6 cm long. This dialysis tube was prewashed before use by boiling in 40% ethanol, and washed with deionized water several times.

Table 1
Operating conditions for ICP-MS and hydride generation-ICP-MS.

Hydride generation conditions	
Concentration of HCl	10% (v/v)
Concentration of $NaBH_4$	1.2% (w/v) (in 0.05%, w/v NaOH)
Concentration of KI	10% (w/v) (in 5%, w/v ascorbic acid)
Flow rate of HCl acid stream	2 mL/min
Flow rate of sample stream	2 mL/min
Flow rate of $NaBH_4$ stream	1 mL/min
Argon carrier gas flow rate	0.99 L/min
ICP-MS: Elan 6000	
Torch	Fassel type with alumina ceramic injector
Nebulizer	Cross-flow
Spray chamber	Cyclonic type
Rf generator frequency	40 MHz
Rf power	1250 W
Nebulizer gas flow rate	0.99 L/min
Coolant gas flow rate	15 L/min
Auxiliary gas flow rate	1.0 L/min
Scanning mode	peak hopping
Isotopes monitored (m/z)	75, 77, 82, 83

2.3. Determination of arsenic content in shrimp sample

To determine the total arsenic content, a known amount of shrimp sample was digested using 5.0 mL of HNO_3 at 100–150 °C. The digestion was performed until the mixture was clear. The digested solution was diluted by deionized water.

For the determination of the dialyzable amount of arsenic in shrimp samples, calibration standards were prepared in sodium bicarbonate of the same concentration as the dialyzing solution.

With hydride generation-ICP-MS determination of arsenic, As (V) was reduced to As (III) prior to analysis by 10% (w/v) potassium iodide solution prepared in 5% (w/v) ascorbic acid to avoid the oxidation of iodide to free iodine by the oxygen [6] in acid medium for 30 min. Arsine was generated and separated from the gas–liquid mixture in the cyclonic spray chamber, and swept with argon gas into the plasma for ionization and measurement of arsenic. The operating conditions of the hydride generation-ICP-MS are summarized in Table 1.

2.4. Simulated gastrointestinal digestion procedure

Simulated gastrointestinal digestion of shrimp was carried out starting with gastric digestion with pepsin, followed by pancreatic digestion with PBE. In the simulated peptic digestion step, 3 g of shrimp on a dry weight basis were added into 8 mL of fruit juices or deionized water and adjusted to pH 2.0 with 6 mol/L HCl. The volume of sample suspension was finally adjusted to 12.5 mL with deionized water and 375 μL of pepsin solution was added. This digestion step was performed in an incubator shaker at 37 ± 1 °C for 2 h. Subsequently, an intestinal digestion and dialysis was performed using a dynamic continuous-flow dialysis system. A portion of the mixture after gastric digestion (2.0 g) was injected into the flattened dialysis bag in the dialysis chamber via a syringe. The dialyzing solution, $NaHCO_3$ of optimum concentration, determined by titratable acidity [16], flowed through the outer surface of the bag at 1 mL/min and the temperature was controlled at 37 ± 1 °C. With the optimum $NaHCO_3$ concentration, the pH of the dialysate was changed from 2 to 5 within the first 30 min. Then, the freshly prepared PBE mixture (625 μL) was added into the dialysis bag and the intestinal digestion and dialysis was continued for additional 90 min. Dialysate fractions were collected at every 10 min for further determination of arsenic by ICP-MS and hydride generation-ICP-MS.

2.5. Calculation of dialyzability

The amount of dialyzed arsenic in dialysate after the simulated gastrointestinal digestion, which is referred to as "bioaccessibility", was expressed as a percentage of the total amount of arsenic present in the sample (dialyzability). The dialyzability was calculated according to the following equation: [26]

$$\text{Dialyzability}\,(\%) = 100\frac{D}{C}$$

where D represents dialyzed arsenic content in dried shrimp sample (μg/kg) and C is the total arsenic content in dried shrimp sample (μg/kg).

3. Results and discussion

3.1. Hydride generation-ICP-MS parameters optimization

Parameters affecting sensitivity of arsenic determination by HG-ICP-MS were examined including the concentrations of HCl, $NaBH_4$, and KI, and the flow rate of acid stream. At fixed $NaBH_4$ flow rate of 1 mL/min, the optimum condition is as follows: 8% (v/v) HCl, 1.0% (w/v) $NaBH_4$, 1.0% (w/v) KI in 5% (w/v) ascorbic acid, with the acid flow rate of 2 mL/min.

The HCl concentrations of 0–30% (v/v) were examined. The lower concentration of HCl gave the lower signal intensities because the reaction was lacked of free hydrogen ions to drive the arsine generation. The signal intensities increased when the HCl concentration was increased from 0% to 8% (v/v), and remained almost constant with the increasing in HCl concentrations above 8% (v/v). Therefore, the HCl concentration of 8% (v/v) was considered optimum.

Not only the concentration of HCl is important, but also its flow rate is also necessary to be optimized. Various acid flow rates of 0.5–3 mL/min were examined and the flow rate of 2 mL/min was selected for this work. Increasing in the acid flow rate resulted in an increased intensity. Nonetheless, too high flow rates led to incomplete reduction of arsenic to arsine gases owing to an inefficient mixing of sample and reagent [6].

The concentration of $NaBH_4$ is also an important parameter for arsine generation. It was used as a reducing and hydride reagent [27–31]. With 8% (v/v) HCl and the acid stream flow rate of 2 mL/min, various concentrations of $NaBH_4$ were investigated in the range of 0–1.8% (w/v) $NaBH_4$ in 0.05 M NaOH. The generation of arsine was improved with increasing in concentration of $NaBH_4$. Nonetheless, with $NaBH_4$ of higher than 1% (v/v), the hydrolysis of $NaBH_4$ generated more hydrogen gas which affected the plasma stability [25]. Therefore, 1.0% (w/v) $NaBH_4$ was found optimum in this work.

In order to guarantee the similarity between the peak height intensities obtained for As(V) and As(III), a pre-reduction of As(V) to As(III) is needed. With peak height measurement, previous studies indicated that the As(V) was characterized by a slowing of hydride formation rate which gave rise to a lower recovery [27–29]. A pre-reduction of As(V) to As(III) was therefore required and was performed by addition of potassium iodide as a reducing agent in combination with ascorbic acid to avoid the oxidation of iodide to free iodine by oxygen [28,29]. In this work, various concentrations of potassium iodide in 5% (w/v) ascorbic acid were examined including potassium iodide of 5–20% (w/v). The signal intensity obtained for As(V) was lower than that of As(III) when the KI concentrations were lower than 10% (w/v). The signal intensities obtained from both species were somewhat equal with the KI concentrations of 10% (w/v) and higher, suggesting that all As(V) was effectively pre-reduced into As(III). Therefore, the KI concentration of 10% (w/v) was chosen in this work. The reaction involved in the pre-reduction step was as follows [32]:

$$H_3AsO_4 + 3I^- + 2H^+ \rightarrow H_3AsO_3 + I_3^- + H_2O$$

3.2. Differentiation of inorganic from organic arsenic with the use of hydride generation-ICP-MS and ICP-MS

With the hydride generation conditions used in this work, hydride generation-ICP-MS was examined for its ability to determine inorganic arsenic, i.e., As(III), As(V), and organic arsenic such as arsenobetaine (AsB). With the arsenic concentrations ranging from 0.25 to 60 μg/L, AsB does not form volatile compounds by reaction with $NaBH_4$, whereas the sensitivity of hydride generation-ICP-MS for As(III) and that for As(V), as considered from the calibration slopes, were nearly the same. The calibration function for As(III) determination was as follows: $y = 3260x - 255$, $R^2 = 0.9998$. The calibration function for As(V) determination was as follows: $y = 3230x - 2140$, $R^2 = 0.9998$. Therefore, hydride generation-ICP-MS, under the conditions used in this work, could be used to detect inorganic arsenic only, by which the responses from As(III) and As(V) were similar.

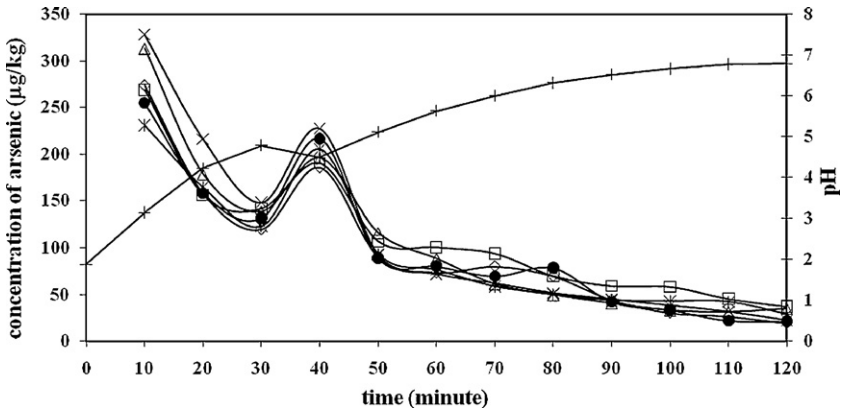

Fig. 2. Dialysis and pH change (+) profiles of arsenic in shrimp without (◊) and with addition of orange juice (□), guava juice (△), apple juice (×), grape juice (●), and ascorbic acid (*) obtained from the continuous-flow dialysis with ICP-MS off-line detection of arsenic.

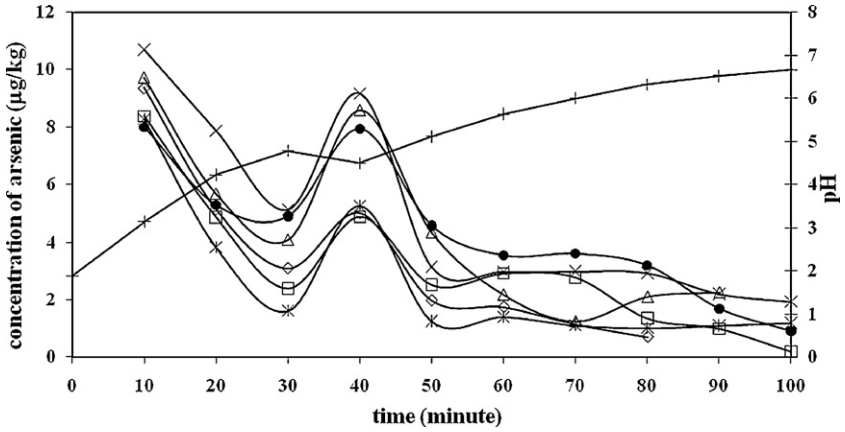

Fig. 3. Dialysis and pH change (+) profiles of arsenic in shrimp without (◊) and with addition of orange juice (□), guava juice (△), apple juice (×), grape juice (●), and ascorbic acid (*) obtained from the continuous-flow dialysis with hydride generation-ICP-MS off-line detection of inorganic arsenic.

Hydride generation-ICP-MS was applied in combination of continuous-flow dialysis for estimation of the bioaccessible amount of inorganic arsenic in shrimp samples. As ICP-MS can detect all forms of arsenic, ICP-MS was applied in combination of continuous-flow dialysis for estimation of the bioaccessible amount of total arsenic in shrimp samples. The differences between the results obtained from the two approaches are considered as a contribution from organic arsenic.

3.3. Application of continuous-flow dialysis for bioaccessibility estimation of arsenic in shrimp samples

With the continuous-flow dialysis method and element detection technique, dialysis profiles were obtained as illustrated in Figs. 2 and 3. They were obtained from the measurement of dialyzed arsenic (Fig. 2, with ICP-MS detection) or dialyzed inorganic arsenic (Fig. 3, with hydride generation-ICP-MS detection). The pH change profiles (Figs. 2 and 3) were also obtained as the pH values of the dialysates were monitored along the digestion process. The pH changes (right axis of Figs. 2 and 3) from approximately 2.0 for gastric digests to approximately 5.0 within 30 min of intestinal digestion and to approximately 7.0 after 90 min were close to what occurs in the human gastrointestinal tract. The dialysis profiles show that the dialyzable arsenic amount was high in the first fraction and gradually decreased as pH increased. The abrupt increase in the dialyzable arsenic at 40 min was due to the addition of PBE at 30 min, suggesting that active enzyme components in PBE helped releasing arsenic which might be bound to large biomacromolecules. Moreover, the inorganic arsenic contents (Fig. 3) were much lower than the total arsenic concentrations (Fig. 2) suggesting that the majority of arsenic was present as organic arsenic. The dialyzable amounts of arsenic and inorganic arsenic in shrimp without addition of ascorbic acid and fruit juices were found to be 1204 µg/kg and 29 µg/kg, respectively.

Further orange juice, guava juice, apple juice, grape juice, and ascorbic acid were examined for their effects on arsenic bioaccessibility in shrimp. As can be seen from Figs. 2 and 3, ascorbic acid and fruit juices did not cause any changes in dialysis profiles. The bioaccessible amounts of total arsenic and inorganic arsenic in shrimp with and without addition of ascorbic acid and fruit juices are summarized in Table 2. The total arsenic content was approximately 2 mg/kg in shrimp sample, therefore under the simulated gastroin-

Table 2
Bioaccessibility of arsenic in shrimp without and with addition of fruit juices and ascorbic acid.

Sample	Bioaccessibility (%)		
	Total arsenic[a]	Inorganic arsenic[b]	Organic arsenic[c]
Shrimp	54.0 ± 2.08	1.23 ± 0.09	52.8 ± 2.39
Shrimp + orange	61.2 ± 4.55	1.34 ± 0.14	59.9 ± 5.21
Shrimp + guava	55.1 ± 4.87	1.58 ± 0.09	53.5 ± 4.36
Shrimp + apple	59.0 ± 4.29	2.31 ± 0.08	56.6 ± 4.94
Shrimp + grape	55.2 ± 2.64	2.01 ± 0.02	53.2 ± 3.03
Shrimp + ascorbic acid	53.4 ± 0.71	1.30 ± 0.15	52.1 ± 0.81

[a] Determined by ICP-MS.
[b] Determined by hydride generation-ICP-MS.
[c] Differences between a and b.

testinal condition used herein the bioaccessibility of arsenic was approximately 55%, with contribution from inorganic arsenic only 1% or 2%, and mostly from organic arsenic. No differences were observed between shrimp without and with addition of fruit juices or ascorbic acid, implying that under the conditions studied herein ascorbic acid and fruit juices used in this study did neither show ability to increase the bioaccessibility of arsenic nor to transform organic arsenic into the more toxic inorganic arsenic form.

4. Conclusions

The combination of continuous-flow dialysis with off-line ICP-MS or hydride generation-ICP-MS detection of arsenic was successfully employed to determine the dialyzable amounts of arsenic or inorganic arsenic in shrimp. The dialyzable amount of organic arsenic in shrimp was deduced from the difference between the concentration values obtained by the two approaches. About half of the arsenic in shrimp was bioaccessible. Further, the arsenic bioaccessibility in shrimp was not increased with addition of ascorbic acid or fruit juices. Also, ascorbic acid or fruit juices did not transform organic arsenic into the more toxic inorganic arsenic form. The continuous-flow dialysis with off-line ICP-MS or hydride generation-ICP-MS detection may be applied to other hydride forming elements to examine their bioaccessibility in other types of food.

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