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# Decomposition of organoarsenic compounds for total arsenic determination in marine organisms by the hydride generation technique

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**The conditions necessary for the complete decomposition of six organic arsenic compounds, namely methylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsine oxide, tetramethylarsonium iodide, arsenocholine bromide (AsC) and arsenobetaine (AB), were investigated. The degree of decomposition of the arsenic compounds was monitored using a hydride generation (HYD) technique, because the response from this system depends strongly on the chemical species of arsenic, with inorganic arsenic (the expected product from these decomposition experiments) giving a much more intense HYD signal than the organic arsenic compounds. The arsenic compounds were decomposed by heating them with three types of acid mixture, namely $HNO_3$–$HClO_4$, $HNO_3$–$HClO_4$–HF, or $HNO_3$–$HClO_4$–$H_2SO_4$. Both MMAA and DMAA were decomposed completely using any of the mixed acids at a decomposition temperature of 200 °C or higher. The $HNO_3$–$HClO_4$–$H_2SO_4$ mixture was the most effective for decomposing AsC and AB, which are the most difficult compounds among all types of organic arsenic compound to decompose and render inorganic. The complete decomposition of AB was only achieved, however, when the temperature was 320 °C or higher, and the sample was evaporated to dryness. When the residue from this treatment was examined by high-performance liquid chromatography combined with inductively coupled plasma atomic emission spectrometry, all of the arsenic was found to be present as arsenic(V). The optimized conditions ($HNO_3$–$HClO_4$–$H_2SO_4$ at 320 °C) for decomposing AB were then used to determine the total amount of arsenic in marine organisms known to contain AB. Copyright © 2005 John Wiley & Sons, Ltd.**

**KEYWORDS:** organic arsenic compounds; wet digestion; microwave digestion; total arsenic

## INTRODUCTION

Arsenite (arsenic(III)) is highly toxic to humans; consequently, many countries have legislation strictly regulating the concentration of arsenic in the environment, and in drinking water and food. Therefore, it is important to determine the concentration of arsenic in the these samples accurately. Widely used analytical techniques for determining arsenic in environmental samples include inductively coupled plasma mass spectrometry (ICP-MS), ICP atomic emission spectrometry (ICP-AES) and electrothermal atomic absorption spectrometry (ETAAS), often in combination with a hydride generation (HYD) system.[1–3]

In addition to arsenic(III) and arsenic(V), several types of organic arsenic compound are also contained in environmental samples, particularly in marine organisms. In general, these organic arsenic compounds are considered to be of low toxicity. Therefore, in the fields of toxicology, environmental science and physiology, it is important to have knowledge about the species of arsenic. Consequently, analytical techniques combining atomic spectrometry and high-performance liquid chromatography, liquid chromatography,

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or capillary electrophoresis have been developed to provide this information.[3,4] However, the accurate determination of the total amount of arsenic in samples is an essential first part of the analytical protocol for the analysis of arsenic species.

Generally, when determining the total amount of arsenic in solid samples an acid digestion procedure is employed to dissolve and completely decompose the sample. Microwave-assisted heating is commonly used for this purpose. The decomposition can be achieved simply and efficiently by microwave-assisted heating because it involves not only acid and heat, but also microwave irradiation and pressure. The application of microwave-assisted heating for the determination of arsenic, however, is not straightforward. Despite several reports on the decomposition of organic arsenic compounds using microwave-assisted heating, the behavior of the various arsenic compounds during this digestion process is still not well understood.[5–11]

An alternative decomposition method is wet acid digestion performed in beakers on a hot plate. This is a common high-quality decomposition procedure that is often reported for the decomposition of organic arsenic compounds. Thus, Jin *et al.*[12,13] used a mixture of nitric acid–perchloric acid–sulfuric acid ($HNO_3$–$HClO_4$–$H_2SO_4$) at 300 °C, and reported that $HClO_4$ was necessary for complete decomposition of arsenobetaine (AB). However, no detailed investigation of the conditions necessary for the complete decomposition of environmental samples has been conducted using wet digestion, and there is a lack of information about the decomposition rate of trimethylarsine oxide (TMAO), tetramethylarsonium iodide (TeMA) and arsenocholine bromide (AsC) under such conditions.

For the decomposition of organic arsenic compounds with microwave-assisted heating, $HNO_3$, $HNO_3$–HCl or $HNO_3$–$HClO_4$ mixtures are often used.[6,7,14] Under these conditions, however, there is a possibility that AB is not completely decomposed, and hence the analysis of samples that contain AB, such as marine organisms, may be compromised.

This is not a problem when using analytical techniques such as ICP-AES or ICP-MS with direct nebulization, because the organic arsenic compounds are decomposed in the high-temperature plasma. Despite the many strengths of ICP-MS, it is expensive instrumentation and its use is still not widespread. ETAAS and ICP-AES, on the other hand, are relatively inexpensive and are commonly used for the determination of arsenic. Moreover, when ETAAS or ICP-AES are combined with HYD, the resulting techniques, HYD-AAS or HYD-ICP-AES, provide low detection limits and are suitable for determining arsenic at environmental concentrations. A major problem, however, is that the efficiency of the generation of arsine (the analyte) is strongly dependent on the type of arsenic species in the sample. Thus, for reliable quantitative data it is essential that the organic arsenic compounds are completely decomposed to inorganic arsenic during the digestion procedure.

In this study, we investigated the conditions required for the decomposition of organic arsenic compounds, with the particular aim of achieving complete decomposition of AB by wet digestion carried out on a hot plate. In addition, we have applied the method to determine the total amount of arsenic in samples containing organic arsenic compounds.

## EXPERIMENTAL

### Apparatus

An ICP-AES Optima 4300DV (Perkin Elmer, Yokohama, Japan) and an ICP-MS 7500C (Agilent, Tokyo, Japan) equipped with a nebulizer and spray chamber were used for arsenic measurements.

A Solaar 989QZ (Unicam, Kyoto, Japan) and an SAS7500A (Seiko Instruments, Chiba, Japan) were used for ETAAS. 989QZ-AA equipped with a graphite atomizer (GFAAS) or quartz cell for HYD, and SPS7500A equipped with a tungsten metal-boat atomizer (MFAAS) furnaces were used. The HYD system was a HYD-10/E90 (Nippon Jarrell-Ash, Kyoto, Japan).

A Chemcosorb 7SAX column (4.6 mm ID × 250 mm, anion-exchange, Chemco Ltd, Tokyo, Japan) with 4 mM $NaH_2PO_4$ (pH 5.3) solution as the mobile phase was used for speciation of arsenic compounds.

Microwave-assisted digestion was performed under controlled pressure conditions with a Milestone MLS 1200 mege (Nihon General Ltd, Tokyo, Japan) equipped with vessels (100 ml capacity) made from tetrafluorometathaxil. An HP30A1 digital hot plate (Luchi Ltd, Osaka, Japan) was used for wet digestion.

### Reagents

An arsenic(III) standard solution was prepared by diluting an AAS-grade commercial arsenic standard solution (1000 mg $l^{-1}$, $As_2O_3$ and NaOH in water, adjusted to pH 5.0 with HCl, Kanto Chemical Industries, Ltd) with water.

An arsenic(V) standard solution was prepared as follows. Precisely 0.458 g of disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, >99%, Wako Pure Chemical Industries, Ltd) was dissolved in water to make a 100 g solution, and the resulting solution was established as a 1000 mg $kg^{-1}$ standard solution of arsenic(V). This standard solution was diluted with water for use in the experiments.

Organic arsenic standards were prepared by dissolving precisely weighed quantities of methylarsonic acid (MMAA, $(CH_3)AsO(OH)_2$, 0.037 g), dimethylarsinic acid (DMAA, $(CH_3)_2AsO(OH)$, 0.037 g), TMAO ($(CH_3)_3AsO$, 0.036 g), TeMA ($(CH_3)_4AsI$, 0.070 g), AsC ($(CH_3)_3As^+CH_2CH_2OH\ Br^-$, 0.065 g) and AB ($(CH_3)_3As^+CH_2COO^-$, 0.048 g) in water to make 20 g solutions. The resulting solutions were established as 1000 mg $kg^{-1}$ (as arsenic) standard solutions of each of the compounds. These standard solutions were diluted with water for use in the experiments.

The acids used were of PMA-grade (Wako Pure Chemical Industries, Ltd) or gravimetric-analysis grade (Kanto Chemical Industries, Ltd). Ultrapure-grade water purified with a Milli Q-Labo filter (Nippon Millipore, Ltd) was used throughout.

## PROCEDURE

### Pretreatment of solid sample by wet digestion

A precisely weighed solid sample (0.5 to 1.0 g) was put into a glass beaker, to which a pre-mixed acid solution ($HNO_3$–$HClO_4$–$H_2SO_4$, $10\,g + 5\,g + 3\,g$) was added. This was placed on a hot plate (instrument set temperature: 320 °C) to dissolve the sample, and the digest solution was then evaporated to dryness. The resulting residue was dissolved in less than 5 g of 1 M HCl and it was made up to 10 to 20 g with water, and the solution obtained was used for the determination of total arsenic.

Blank tests carried out under the same digestion conditions were performed with each batch of samples, but no arsenic contamination was found.

## RESULTS AND DISCUSSION

### Relative responses of arsenic compounds determined by different measurement methods

The responses of eight arsenic compounds (arsenic(III), arsenic(V), MMAA, DMAA, TMAO, TeMA, AsC and AB) were compared for each of the measurement methods. Table 1 shows the analysis conditions optimized for each instrument, and the results obtained are shown in Table 2. The relative responses were calculated on the basis of values for arsenic(III) determined for each instrument. When ICP-AES and ICP-MS were used, the responses for all eight arsenic species were essentially the same (approximately 5% variability). This is because the high-temperature plasma has sufficient energy to decompose the various arsenic compounds completely.

For GFAAS, it is impossible to retain arsenic in the graphite furnace at high pyrolysis temperatures without the addition of chemical modifiers. When GFAAS was used as the measurement method, the difference in relative responses for the organic arsenic compounds ranged from 20 to 80% due to variable thermal decomposition and losses of the arsenic species at the pyrolysis stage. The problem was greatly reduced by adding Pd–$Mg(NO_3)_2$, a commonly used

**Table 1.** Instrumental operating parameters for arsenic

| | | | |
|---|---|---|---|
| *ICP-AES* | | *ICP-MS* | |
| Wavelength (nm) | 188.98 | Acquired mass | 75 |
| RF power (kw) | 1.4 | RF power (kw) | 1.5 |
| Plasma gas flow rate ($l\,min^{-1}$) | 15 | Plasma gas flow rate ($l\,min^{-1}$) | 15 |
| Aux. gas flow rate ($l\,min^{-1}$) | 0.2 | Aux. gas flow rate ($l\,min^{-1}$) | 0.9 |
| Carrier gas flow rate ($l\,min^{-1}$) | 0.6 | Carrier gas flow rate ($l\,min^{-1}$) | 1.2 |
| Nebulizer | Coaxial glass | Nebulizer | Teflon |
| Spry chamber | Cyclone | Spry chamber | Quartz |
| Observation | Axial | Sample depth (mm) | 7 |
| *GFAAS* | | *MFAAS* | |
| Wavelength (nm) | 193.7 | Wavelength (nm) | 193.7 |
| Dry 1 (°C) | 110 | Dry (°C) | 130 |
| Dry 2 (°C) | 150 | | |
| Pyrolysis (°C) | 1000 | Pyrolysis (°C) | 1000 |
| Atomize (°C) | 2300 | Atomize (°C) | 2500 |
| Clean (°C) | 2400 | Clean (°C) | 2600 |
| Lamp current (mA) | 12 | Lamp current (mA) | 10 |
| Gas flow rate ($l\,min^{-1}$) | Ar: 0.3 | Gas flow rate ($l\,min^{-1}$) | Ar: 5.0/$H_2$: 1.0 |
| Atomizer | Graphite | Atomizer | Tungsten |
| BKG correction | Zeeman | BKG correction | $D_2$ |
| Chemical modifier | Pd–$Mg(NO_3)_2$ | Chemical modifier | Cobalt(III) oxide |
| *HYD* | | *HPLC* | |
| Acid | 6M HCl | Column | Chemcosorb-7SAX |
| Aux | 40% KI | Mobile phase | 4mM $NaH_2PO_4$–0.5%$CH_3OH$ |
| $NaBH_4$ | 1% | pH | 5.3 |
| Sample flow speed ($ml\,min^{-1}$) | 5.0 | Flow rate ($ml\,min^{-1}$) | 1.0 |
| Furnace temperature (°C) (HYD-ASS) | 1000 | Injection volume (μl) | 200 |

**Table 2.** Relative sensitivity of arsenic compounds on each instrument

| As compound | ICP-AES | ICP-MS | GFAAS (modifier added[a]) | HYD-ICP-AES | HYD-AAS |
|---|---|---|---|---|---|
| As(III) | 100.0 ± 0.5 | 100.0 ± 0.2 | 100.0 ± 0.3 | 100.0 ± 0.4 | 100.0 ± 0.2 |
| As(V) | 100.1 ± 0.5 | 100.9 ± 0.2 | 99.3 ± 0.3 | 85.6 ± 1.6 | 109.3 ± 1.5 |
| MMAA | 95.3 ± 0.6 | 99.5 ± 0.2 | 99.0 ± 0.3 | 145.5 ± 2.5 | 103.0 ± 1.3 |
| DMAA | 102.0 ± 0.5 | 102.5 ± 0.3 | 97.8 ± 0.4 | 35.6 ± 2.8 | 39.5 ± 1.7 |
| TMAO | 104.3 ± 0.6 | 100.2 ± 0.3 | 96.8 ± 0.6 | 1.7 ± 1.3 | ND |
| TeMA | 100.0 ± 0.5 | 100.2 ± 0.3 | 96.0 ± 1.0 | 6.9 ± 1.8 | ND |
| AB | 96.8 ± 0.8 | 104.2 ± 0.5 | 95.9 ± 1.5 | ND | ND |
| AsC | 95.0 ± 0.7 | 103.9 ± 0.4 | 97.7 ± 1.5 | ND | ND |

[a] Pd–$Mg(NO_3)_2$.

chemical modifier for analysis of arsenic by GFAAS. This reduced the variability in response between the various arsenic species to less than 9%.

The differences in the relative responses for the arsenic species determined using the HYD-combined measurement method were significant. Each of the species behaves differently when subjected to the HYD reaction conditions, and they show markedly different efficiencies at generating the volatile arsine that serves as the analyte. Under the conditions employed in our study, arsenic(III) is the species most efficiently converted to arsine; accordingly, it gives the greatest response, whereas AB and AsC do not produce an arsine at all.

Because of these differences in behavior of the various arsenic species, errors are expected when ETAAS or HYD-combined measurement methods are used to determine arsenic concentrations in environmental samples. To overcome these problems, it is necessary that organic arsenic compounds present in environmental samples are completely decomposed in the pretreatment to a common arsenic species. In most cases when oxidizing conditions are employed, this species will be the most oxidized form of inorganic arsenic.

## Decomposition of arsenic compounds using microwave-assisted heating

We monitored the decomposition of the various arsenic compounds subjected to acid digestion and microwave-assisted heating by using HYD-ICP-AES to measure the responses for arsenic in the digests relative to the response for arsenic(III). In this experiment, one of the most simple procedures was applied. Thus, nitric acid was used to decompose the samples, and the heating program was set to 250 W for 2 min, 0 W for 2 min, 400 W for 5 min and 650 W for 5 min. The maximum temperature was 250 °C. The results obtained in this experiment are shown in Table 3. Under these conditions, the response for AB was only approximately 4% of that obtained for arsenic(III), which indicates that AB was poorly decomposed. In addition, the total amount of arsenic in certified reference materials (CRMs) DORM-2 (dogfish muscle), TORT-2 (lobster hepatopancreas), and NIES No.15 (scallop) was determined by HYD-ICP-AES after the samples were digested using these microwave-assisted conditions (Table 4). The amount determined, however, differed significantly from the certified value in each CRM due to insufficient decomposition of AB. Hence, it was necessary to examine in detail the conditions required for the complete decomposition of organic arsenic compounds.

**Table 3.** Recovery (%) of spiked arsenic compounds when heated in microwave with $HNO_3$

| As compound | HYD-ICP-AES |
|---|---|
| As(III) | 100.0 ± 0.5 |
| As(V) | 99.5 ± 1.5 |
| MMAA | 103.8 ± 16.3 |
| DMAA | 45.4 ± 1.0 |
| TMAO | 53.1 ± 7.5 |
| TeMA | 50.8 ± 5.5 |
| AB | 5.0 ± 2.7 |
| AsC | 53.1 ± 6.9 |

## Decomposition of arsenic compounds by wet digestion

The acid and temperature conditions necessary to decompose organic arsenic compounds by wet digestion were investigated. Three different acid mixtures, $HNO_3$–$HClO_4$ (10 g + 5 g), $HNO_3$–$HClO_4$–HF (10 g + 5 g + 3 g), or $HNO_3$–$HClO_4$–$H_2SO_4$ (10 g + 5 g + 3 g), were added to sample solutions containing 20 μg $kg^{-1}$ (as arsenic, 0.2 μg/10 g) of organic arsenic compounds and tested at arbitrary temperatures. The samples were heated on the hot plate until the acids had evaporated to dryness. The residues obtained after the decomposition and evaporation steps were dissolved using less than 5 g of 1 M HCl solution, and this was made up to 10 g with water. The solutions were then analyzed for arsenic by HYD-ICP-AES, which provides a measure of the degree of decomposition, as described above.

For the $HNO_3$–$HClO_4$–HF mixture it was necessary to use Teflon beakers, and the maximum temperature was set at 280 °C. For the other two acid mixtures, glass beakers were used and the maximum temperature was set at 380 °C.

Table 4. Results of total arsenic determined by ICP-AES and HYD-ICP-AES

| Sample ($n = 5$) | Digestion | Mean total As/μg g$^{-1}$ ICP-AES | Mean total As/μg g$^{-1}$ HYD-ICP-AES | Certified or reference value/μg g$^{-1}$ |
|---|---|---|---|---|
| DORM2 | Wet[a] | 19.1 ± 0.8 | 1.2 ± 0.2 | 18.0 ± 1.1 |
| Dogfish muscle | Microwave[b] | 18.5 ± 0.4 | 1.2 ± 0.1 | |
| TORT2 | Wet[a] | 22.0 ± 0.9 | 3.8 ± 0.2 | 21.6 ± 1.8 |
| Lobster hepatopancreas | Microwave[b] | 16.1 ± 0.3 | 2.6 ± 0.1 | |
| NIES No.14 | Wet[a] | 67.4 ± 0.2 | 67.3 ± 0.4 | 66 ± 75[c] |
| Brown alga *(Hijiki)* | Microwave[b] | 67.2 ± 0.4 | 67.1 ± 0.6 | |
| NIES No. 15 | Wet[a] | 3.42 ± 0.06 | 0.36 ± 0.05 | 3 ± 4[c] |
| Scallop | Microwave[b] | 3.36 ± 0.05 | 0.39 ± 0.04 | |

[a] With $HNO_3$–$HClO_4$, using hot plate (230 °C).
[b] With $HNO_3$(200 °C).
[c] Reference value.

At first, we measured the set temperature of the hot plate and the inside (bottom) temperature of the beaker by using a thermometer equipped with a probe. Each set of temperatures was corrected to the target value of the inside temperature of the beaker. Therefore, the decomposition temperatures used the set value. The results are shown in Fig. 1.

We thought it possible that losses of arsenic due to volatilization may occur during evaporation to dryness. Our results, however, show that this was not the case, because, even at the highest acid decomposition temperature of 380 °C, the recovery of arsenic(III) and arsenic(V) was 100% (Fig. 1a). DMAA appeared to be completely decomposed in our wet digestion experiments, as shown by the increased response in the HYD-ICP-AES measurement; whereas the response for DMAA was 35.6% before the acid decomposition (Table 2), it was 100% after the acid treatment. (Fig. 1b).

In contrast, AB was not decomposed completely with $HNO_3$–$HClO_4$ over a temperature range of 200 to 380 °C, or with the use of $HNO_3$–$HClO_4$–HF over a range of 200 to 280 °C. The maximum response obtained by HYD-ICP-AES was approximately 50% of that for arsenic(III); since intact AB gives no response by this technique, the results indicate that decomposition occurred to a maximum of 50%. However, when the mixture of $HNO_3$–$HClO_4$–$H_2SO_4$ was used over a temperature range of 320 to 380 °C, complete decomposition of AB was achieved 100% (Fig. 1b).

## Confirmation of arsenic species in the digest solutions by HPLC–ICP-AES

Marine animals generally contain a large amount of AB.[15] The CRM NIES No.15 (scallop) was chosen for further investigation because previous work had demonstrated the presence of AB in this sample.[16]

Water-soluble arsenic compounds were extracted from the scallop sample. A portion of the extract containing the water-soluble arsenic compounds was analyzed directly by

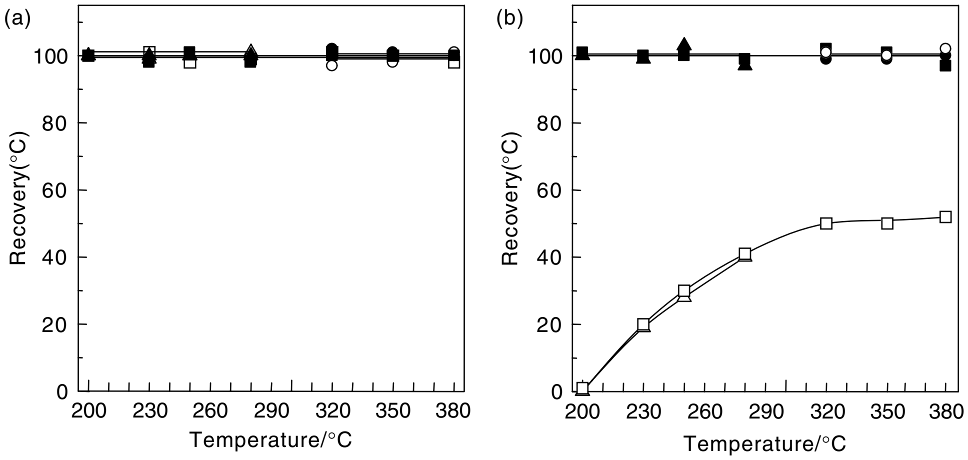

Figure 1. Decomposition rate of arsenic compounds when heated on a hot plate with mixed acids. Method: HYD-ICP-AES. (a) ▲, ■, ●: arsenic(III); △, □, ○: arsenic(V); ▲, △: $HNO_3$–$HCl_4$–HF; ■, □: $HNO_3$–$HClO_4$; ●, ○: $HNO_3$–$HClO_4$–$H_2SO_4$. (b) ▲, ■, ●: DMAA; △, □, ○: AB; ▲, △: $HNO_3$–$HClO_4$–HF; ■, □: $HNO_3$–$HClO_4$; ●, ○: $HNO_3$–$HClO_4$–$H_2SO_4$.

HPLC–ICP-AES, and other portions were decomposed with $HNO_3$–$HClO_4$ or $HNO_3$–$HClO_4$–$H_2SO_4$ mixtures at various temperatures, and the decomposition products analyzed by HPLC–ICP-AES. The data, shown as chromatograms in Fig. 2, confirm the previously reported presence of AB in the extract from the scallop sample.[17]

In the digest solution obtained from using $HNO_3$–$HClO_4$ and a hot plate at a temperature of 200 °C, undecomposed AB and arsenic(V) were observed, which was generated from the partial decomposition of AB. The decomposition of AB was not complete under these conditions (Fig. 2b (b)). The digest solution obtained from using $HNO_3$–$HClO_4$–$H_2SO_4$ and a hot plate at a temperature of 320 °C, however, contained only one peak corresponding to arsenic(V), and the peak corresponding to AB had disappeared (Fig. 2b (c)). These results, which confirm the conversion of AB to arsenic(V) upon the addition of the acid, agreed with the results of Goessler and co-workers.[5,6]

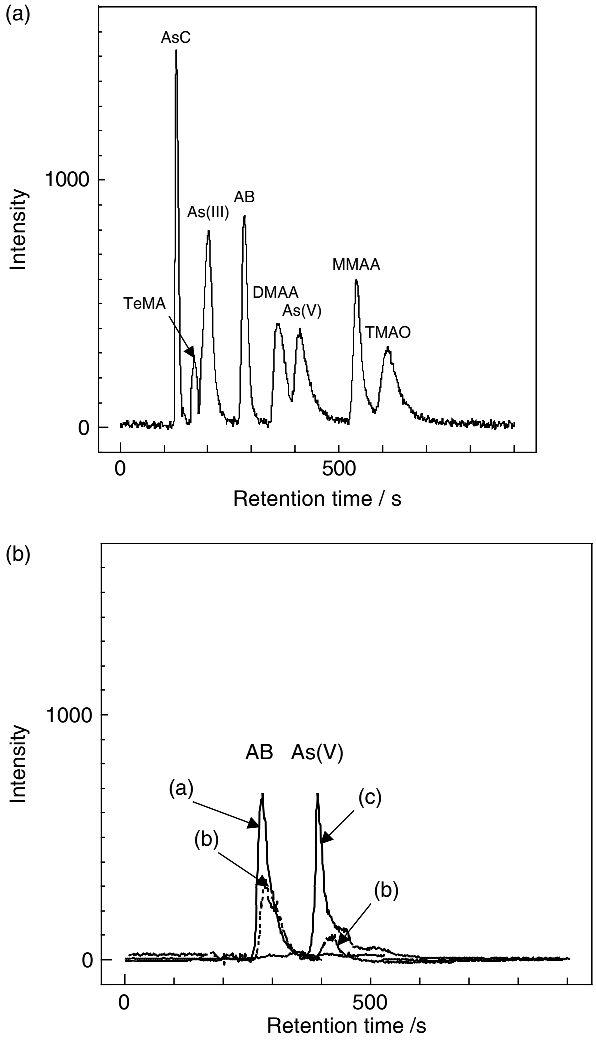

**Figure 2.** Anion-exchange chromatograms. (a) Standard solution. Conditions: Chemcosorb 7SAX column (4.6 mm × 250 mm), 4 mM $NaH_2PO_4$–0.5% $CH_3OH$ (pH 5.3), flow rate 1.0 ml $min^{-1}$, injection volume 200 μl, arsenic compounds 0.1 mg $l^{-1}$. (b) From digests of NIES No.15 when heated to different temperatures and with mixed acids. Conditions: Chemcosorb 7SAX column (4.6 mm × 250 mm), 4mM $NaH_2PO_4$–0.5% $CH_3OH$ (pH 5.3), flow rate 1.0 ml $min^{-1}$, injection volume 200 μl, arsenic compounds 0.1 mg $l^{-1}$. (a) water-soluble arsenic, (b) wet digestion with $HNO_3$–$HClO_4$ (200 °C), (c) wet digestion with $HNO_3$–$HClO_4$–$H_2SO_4$ (320 °C).

When $HNO_3$ or $HNO_3$–$HClO_4$ was used, however, the conversion of AB to arsenic(V) was only approximately 60% in the temperature range between 300 and 320 °C. In accordance with this result, we conclude that the conditions necessary for complete decomposition are the addition of $HNO_3$–$HClO_4$–$H_2SO_4$ and a decomposition temperature of 320 °C. In addition, we confirmed that it was possible for microwave-assisted heating to AB completely decompose with the addition of $HNO_3$–$HClO_4$–$H_2SO_4$ at a temperature of 300 °C.

## Application to real samples

Wet digestion was applied to real samples to determine the total arsenic concentration. NIST1548a (typical diet) was chosen for this study, because it appears to contain various components of the human diet and arsenic compounds. Three samples rich in AB, namely DORM-2 (dogfish muscle), TORT-2 (lobster hepatopancreas), and NIES No.15 (scallop), in addition to NIES No.14 (brown alga) containing inorganic arsenic and an arsenic sugar, were also used in this part of the study.[16] The samples (0.5 to 1.0 g) were digested with the $HNO_3$–$HClO_4$–$H_2SO_4$ mixture at 320 °C, and then diluted before the arsenic content was determined. To confirm that the organic arsenic compounds were completely decomposed, the amount of arsenic in each sample was determined by ICP-AES, MFAAS, which included a pretreatment step of solid-phase extraction,[17] and HYD-ICP-AES. The results obtained are shown in Table 5. The total arsenic concentrations in all five reference materials were consistent with the certified values regardless of the method of determination.

## CONCLUSIONS

We investigated methods for decomposing organic arsenic compounds necessary to determine the total amount of arsenic accurately. The conventional decomposition method, wet digestion using a hot plate, was studied in detail. We showed that the acid combination $HNO_3$–$HClO_4$–$H_2SO_4$ and heating at a temperature above the boiling point of $H_2SO_4$ was essential to decompose AB completely (the most difficult organic arsenic compound) to arsenic(V).

Since we have not investigated the necessity of inclusion of $HClO_4$ in the acid combination, which is controversial,[12,18] further study is needed to clarify its necessity if we consider

**Table 5.** Results of total arsenic determined using hot plate method with $HNO_3-HClO_4-H_2SO_4$

| Sample (n = 6) | Method | Mean total As/μg $g^{-1}$ | Certified or reference value/μg $g^{-1}$ |
|---|---|---|---|
| NIST1548a | MFAAS | 0.20 ± 0.01 | 0.20 ± 0.01 |
| Typical diet | ICP-AES | 0.22 ± 0.02 | |
| | HYD-ICP-AES | 0.19 ± 0.03 | |
| DORM2 | MFAAS | 18.1 ± 0.3 | 18.0 ± 1.1 |
| Dogfish muscle | ICP-AES | 18.6 ± 0.4 | |
| | HYD-ICP-AES | 18.3 ± 0.6 | |
| TORT2 | MFAAS | 22.3 ± 1.1 | 21.6 ± 1.8 |
| Lobster hepatopancreas | ICP-AES | 21.4 ± 0.8 | |
| | HYD-ICP-AES | 21.9 ± 1.2 | |
| NIES No.14 | MFAAS | 67.8 ± 0.3 | 66 ± 75[a] |
| Brown alga (*Hijiki*) | ICP-AES | 67.5 ± 0.1 | |
| | HYD-ICP-AES | 67.7 ± 0.6 | |
| NIES No.15 | MFAAS | 3.57 ± 0.03 | 3 ± 4[a] |
| Scallop | ICP-AES | 3.55 ± 0.02 | |
| | HYD-ICP-AES | 3.51 ± 0.04 | |

[a] Reference value.

the potential danger associated with $HClO_4$ usage. Until such time, we should follow the safe handling instructions for use of $HClO_4$ by Graf.[19]

These conditions are suitable for both heating on a hot plate and with microwave-assisted heating. The conditions necessary for the decomposition of AB can also be successfully applied to other arsenic compounds. However, there is a possibility that these conditions will have different influences on the matrix elements for different samples. Further investigations utilizing the standard addition method are necessary to validate analytical techniques employing HYD and other pretreatment procedures.

## REFERENCES

1. Evans EH, Day JA, Price WJ, Smith CMM, Suttone K, Tyson JF. *J Anal. At. Spectrom.* 2003; **18**: 808.
2. Matusiewicz H, Kopras M. *J. Anal. At. Spectrom.* 2003; **18**: 1415.
3. Evans EH, Dawson JB, Fisher A, Price WJ, Smith CMM, Tyson JF. *J. Anal. At. Spectrom.* 2002; **17**: 622.
4. Bacon JR, Greenwood JC, Vaeck LV, Williams JG. *J. Anal. At. Spectrom.* 2003; **18**: 955.
5. Goessler W, Pavkov M. *Analyst* 2003; **128**: 796.
6. Wasilewska M, Goessler W, Zischka M, Maichin B, Knapp G. *J. Anal. At. Spectrom.* 2002; **17**: 1121.
7. Deaker M, Maher W. *J. Anal. At. Spectrom.* 1999; **14**: 1193.
8. Chatterjee A. *J. Anal. At. Spectrom.* 2000; **15**: 753.
9. Burguera M, Burguera JL. *Anal. Chim. Acta* 1998; **366**: 63.
10. Santos C, Moreno FA, Lavilla I, Bendicho C. *J. Anal. At. Spectrom.* 2000; **15**: 987.
11. Smith FE, Arsenault EA. *Talanta* 1996; **43**: 1207.
12. Jin K, Ogawa H, Taga M. *Bunseki Kagaku* 1983; **32**: E171.
13. Jin K, Ogawa H, Taga M. *Bunseki Kagaku* 1983; **32**: E259.
14. Abu-Samra A, Morris JS, Koirtyohann SR. *Anal. Chem.* 1975; **47**: 1475.
15. Ackley KL, B'Hymer C, Sutton KL, Caruso JA. *J. Anal. At. Spectrom.* 1999; **14**: 845.
16. Yoshinaga J, Shibata Y, Horiguchi T, Morita M. *Accredit. Qual. Assur.* 1997; **2**: 154.
17. Narukawa T, Yoshimura W, Uzawa A. *Bull. Chem. Soc. Jpn.* 1999; **72**: 701.
18. Slejkovec Z, van Elteren JT, Woroniecka UD. *Anal. Chim. Acta* 2001; **443**: 277.
19. Graf FA. *Chem. Eng. Prog.* 1966; **62**: 109.