Preliminary Results of Extraction, Separation and Quantitation of Arsenic Species in Food and Dietary Supplements by HPLC-ICP-MS

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Various extraction procedures were investigated using reference materials and samples to evaluate extraction efficiency and effectiveness. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure total arsenic and to quantitate arsenic species when coupled to an HPLC (high pressure liquid chromatography). Arsenic species were extracted from rice flour (NIST SRM 1568a) with water/methanol mixtures using accelerated solvent extraction (ASE). Total arsenic extraction efficiency ranged from 42 to 64%, for water and various methanol concentrations. From spinach (NIST SRM 1570), freeze-dried apple, and rice flour (NIST SRM 1568a), arsenic species were extracted with trifluoroacetic acid (TFA) at 100 °C. Total arsenic extraction efficiency was 90% for spinach, 75% for freeze-dried apple, and 83% for rice flour. Enzymatic extraction with alpha-amylase and sonication resulted in extraction efficiency of 104% for rice flour, 98% for freeze-dried apple, and 7% for spinach. Chromatograms of arsenic species extracted by the optimum extraction methods were obtained, and the species were quantified. Arsenite (As(III)), arsenate (As(V)), dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA) were found in the apple sample, and DMA and As(V) in the rice flour sample. As(V) and MMA were found in three herbal dietary supplement samples.

Key Words : Arsenic speciation, HPLC, ICPMS, Food, Dietary supplement

Introduction

The toxic element arsenic is monitored in food and dietary supplements to assess exposure.[1-3] Most routine analyses provide the total arsenic concentration, but the toxic and biological effects of arsenic are dependant on its chemical form. Thus, speciation of arsenic in food and dietary supplements is necessary to provide a meaningful assessment of exposure. Chemical speciation of an element involves quantitative determination of the different chemical forms. The forms can differ by oxidation state, inorganic versus organic form, and varying organic ligands.[4-13]

As(III) is the most toxic inorganic species commonly found in environmental and biological samples. As(V) is also toxic, but less so than As(III). There are many organic forms including species such as methylarsonic acid (MMA) and dimethylarsinic acid (DMA).[13] Methylated arsenic species have been known to be much less toxic than the inorganic species. Therefore, in order to conduct a proper arsenic risk assessment, the various arsenic species should be identified and their concentrations determined in food and dietary supplements.

Over the years, many investigators have reported arsenic speciation using various techniques.[10-26] However, arsenic speciation is still challenging for several reasons. The integrity of arsenic species must be maintained during sample extraction, preparation and storage. There are few reference materials (RMs) available for the various arsenic species even though there is the need for accurate measurement of these species. Finally, there is no single satisfactory method for extracting arsenic species from foods.

In this research, various extraction methods were investigated for extraction efficiency. Accelerated solvent extraction (ASE),[11] trifluoroacetic acid (TFA),[11,27,28] and enzyme (amylase/sonication) extraction[8,11] were used to extract arsenic from rice flour, freeze-dried apple, spinach and herbal dietary supplements. Although ion-pair reversed-phase HPLC has been used by other researchers,[29] greater success has been obtained with anion-exchange columns. The Hamilton PRP-X100 anion-exchange column has been used successfully to separate As(III), As(V) and various organic arsenic species.[8,27,30,31] The chromatography in this work was carried out using isocratic HPLC with an ammonium carbonate mobile phase and a PRP-X100 column.[32] Although a gradient system might result in better separation, isocratic conditions were chosen for better compatibility with the ICP-MS technique.[8,33] Ammonium carbonate buffer was chosen over other possibilities because it leaves minimal deposits on the interface cones and lenses of the ICP-MS.[32] Chromatograms of arsenic species extracted by the optimum extraction methods were obtained, and the species were quantified. For dietary supplements, the work focused on the quantitation of inorganic arsenic species (As(III) and As(V)) due to their toxicity.

Experimental Section

Instrumentation. HPLC (Waters 2690 Separation module, Waters, Milford, MA, USA) system was used with a 150 mm × 4.1 mm (id) Hamilton PRP-X100 anion exchange

column (Hamilton, Reno, NV). The eluent (mobile phase) was 30 mM ammonium carbonate buffer solution adjusted to pH 8.5 with dilute ammonium hydroxide. Flow rate was 1.0 mL min^{-1} and injection volume was 25 μL. Effluent was transferred to a PEEK Mira Mist nebulizer (Burgener Research Inc.) using a 6-inch length of PEEK 1/16" OD × 0.020" ID tubing with PEEK finger tight fittings (Upchurch Scientific, Oak Harbor, WA). ICP-MS (Agilent 7500c ICP-MS, Agilent, Palo Alto, CA) with a quartz double pass spray chamber. Operating parameters: forward power: 1500 W, coolant gas flow: 15 L min^{-1}, auxiliary gas flow: 1.0 L min^{-1}, nebulizer gas flow: 1.2 L min^{-1}, Mass monitored: 75 m/z, Integration time: One second/point. Accelerated Solvent Extractor: Dionex ASE 200 (Dionex Corp., Sunnyvale, CA). Operating parameters: 11 mL cell size, 1500 psi pressure, 10 min static time, 100% flush, 90 sec purge, temperature: 100 °C, 40 °C, preheat: 5 min, heat: 5 min.

A SpeedVac Concentrator (Thermo Savant SPD131DDA, San Jose, CA) was used to concentrate analyte in the extracts.

Chemicals and reagents. 1000 mg L^{-1} As(III) and 1000 mg L^{-1} As(V) standards were obtained from Spex CertiPrep (Metuchen, NJ, USA). Dimethylarsinic acid (DMA) was obtained from Sigma-Aldrich (St Louis, MO, USA). Methylarsonic acid (MMA)was obtained from Chem Service (West Chester, PA, USA). Arsenobetaine (AsB) solution (1031 mg kg^{-1}, BCR-626) was obtained from European Commission Community Bureau of Reference. Ultrapure deionized water (DIW) was obtained from a Milli-Q Element system (Millipore, Bedford, MA, USA). High-purity ammonium carbonate, ammonium hydroxide, and acetic acid were purchased from J.T. Baker (Phillipsburg NJ, USA). Trifluoroacetic acid was purchased from Alfa Aesar (Ward Hill, MA, USA) and α-amylase was purchased from Sigma Chemical Co.

Dietary supplements.

• Sample 1 labeled ingredients: astragalus root extract, rosemary leaf extract, orange peel extract, turmeric root extract, red clover flower extract (plus 10 other extracts)

• Sample 2 labeled ingredients: ginseng mixture (Siberian, Chinese, American, and Korean)

• Sample 3 labeled ingredients: red clover blossoms, echinacea, licorice root, buckhorn bark and burdock root.

Determination of total extracted arsenic. Total arsenic in extracts was determined by ICP-MS analysis after dilution in 1% nitric acid. Depending on the extract, dilution factors between 200 and 400 were used to minimize matrix interference and build-up on the sampler cone. Aliquots of diluted extracts were fortified at approximately 1 to 2 times the unfortified levels and analyzed. Fortification recoveries of 90-110% indicated lack of matrix interference. To account for potential $^{40}Ar^{35}Cl$ and $^{40}Ca^{35}Cl$ isobaric interferences on ^{75}As, the reaction cell was used in collision mode with helium gas.

Determination of total arsenic. Total arsenic in samples was determined by ICP-MS after closed-vessel microwave digestion (Mars 5, CEM Corporation, Matthews, NC, USA). Portions of samples (0.5 g) and nitric acid (10 mL) were added to Teflon® TFM liners and immediately sealed in the digestion vessel. Samples were subjected to a 3-step temperature controlled program with a final stage of 200 °C for 10 minutes. After cooling, digests were transferred to polypropylene centrifuge tube and diluted to 50 mL with DIW. Aliquots of digestion solutions were further diluted in 1% nitric acid prior to analysis by ICP-MS. Helium collision gas was used to eliminate potential isobaric interferences.

Extraction efficiency was calculated as the ratio of total extracted arsenic to total arsenic in samples.

Results and Discussion

Extraction of arsenic in rice flour by ASE. Three cycles of extraction using 10 mL of solvent each time was performed at 40 °C. The resulting extracted volumes were 13.6, 13.5, 23.5, 20.6 mL with DIW and 0, 25, 50, 100% MeOH, respectively. Extracts were diluted by a factor of 200 before total arsenic analysis by ICP-MS. Extraction efficiencies were 64, 65, 58 and 42% for 0, 25, 50 and 100% MeOH, respectively. Portions (5 mL) of all four sample extracts extractsewere subjected to the SpeedVac (45 °C) for solvent removal and then reconstituted to 5 mL with DIW for analysis of total arsenic. Water was chosen in an attempt to maintain chemical integrity of the extracted arsenic. Apparent extraction efficiencies measured in the reconstituted extracts were 58, 56, 52 and 40% for 0, 25, 50 and 100% MeOH, respectively. The above results show that some analyte might be lost in the process of removing solvent from extracts.

Three cycles of extraction using 10 mL of solvent each time was then performed at 100 °C. The resulting extracted volumes were 25.5, 24.0, 7.2, 19.0 mL with 0, 25, 50, 100% MeOH, respectively. The extraction volume obtained by 50% MeOH was much less than the other extraction volumes. The experiment was repeated, but the same volume was obtained for reasons that cannot be explained at the present time. The extracts were diluted by a factor of 250 for analysis. Extraction efficiencies were 27, 22, 45 and 55% for 0, 25, 50 and 100% MeOH, respectively. Portions (5 mL) of all four sample extracts were concentrated by SpeedVac (45 °C) and reconstituted to 5 mL with DIW. Apparent extraction efficiencies were 27, 19, 5.4 and 50% for 0, 25, 50 and 100% MeOH, respectively.

Extraction efficiency at both temperature conditions was less than desired and less than what others have reported.[11] The reason why the ASE did not work as well as expected is unclear. More research is planned to investigate the lower than expected efficiency and the apparent loss during solvent evaporation.

Extraction of arsenic with TFA. Although various ratios of methanol-water are commonly used for arsenic extraction, TFA has also been used as an efficient solvent for arsenic extraction.[11,27] However, Abedin *et al.*[27] found that up to 20% of the As(V) can be reduced to As(III) during extraction with TFA. Therefore, a TFA extraction should not be used to obtain exact ratios of As(III) to As (V). Rice flour (2 g) was suspended in 6 mL of 2 M TFA at room temper-

ature for 48 hours. The extract was filtered through a 0.45 μm filter. Additional portions were prepared and kept in the oven at 100 °C for 4 and 6 hours, then filtered through a 0.45 µm filter.

The three extracts were diluted by a factor of 400 and analyzed by ICP-MS. Portions of diluted extracts were spiked (0.1 µg L^{-1} As) to check for matrix interference. The recovery was 104% and 101% for room temperature (48 hr) and 100 °C (4 hr), respectively. Total arsenic extraction efficiencies were 73%, 80%, and 83% at room temperature (48 hr), 100 °C (4 hr), and 100 °C (6 hr), respectively. Portions of extracts were concentrated by SpeedVac (45 °C) for 2 hours, diluted with DIW and re-analyzed for total arsenic by ICP-MS. Apparent extraction efficiencies were 15%, 16% and 70%, respectively. The results show that some arsenic was lost in the process of removing TFA from extracts. Further research is planned to investigate the apparent loss.

For comparison, 1 g samples of spinach and freeze-dried apple were suspended in 10 mL of 2 M TFA. Solutions were kept at 100 °C for 6 hours, and then filtered through a 0.2 µm filter for analysis. Total arsenic extraction efficiency for spinach was 88% (calculated from certified value) and 92% (calculated from total arsenic value determined by ICP-MS after microwave digestion). Total arsenic extraction efficiency for freeze-dried apple was 75%.

Enzyme extraction (amylase/sonication extraction). Enzyme extraction using α-amylase was also tried using the method described by B'Hymer and Caruso.[8] The method was performed as follows:

1) 0.5 g sample aliquots were treated with 30 mg of α-amylase in 10 mL of 0.1 M solution of ammonium carbonate, pH adjusted to approximately 7.2 by the addition of 6 M acetic acid.

2) Solutions were allowed to react overnight while being swirled at constant temperature of 37 °C.

3) 8.0 mL of acetonitrile and 2.0 mL of water were added to each sample followed by sonication for six hours.

4) Solutions were transferred to centrifuge tubes and spun at 2500 rpm for five minutes.

5) The supernatant was collected and the solid residue was washed with 5 mL of 40/60 (V/V) acetonitrile/water. Solutions were combined.

6) Solvents were removed in the SpeedVac Concentrator.

7) Residues were diluted to 5 mL with mobile phase and filtered through 0.2 µm nylon filters.

The extraction efficiency of total arsenic in rice flour, freeze-dried apple, and spinach were 104 (from certified value), 98%, and 7%, respectively.

Table 1. Comparison of total arsenic extraction efficiency from rice flour, freeze-dried apple, and spinach with enzyme extraction and TFA (100 °C for 8 hours)

	Rice flour (NIST SRM 1568a)	Spinach (NIST SRM 1570)	Freeze-dried apple
Enzyme	104%	7 %	98%
TFA	83%	88-92%	75%

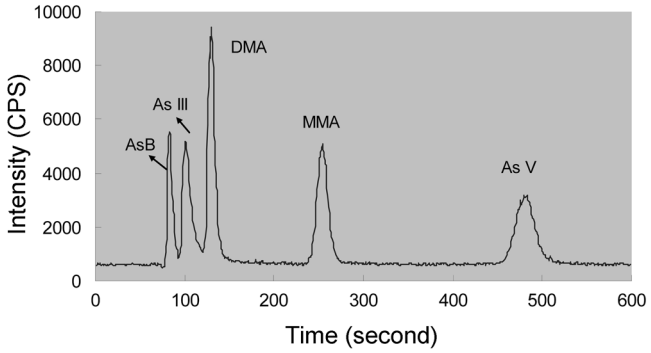

Figure 1. HPLC-ICP-MS chromatogram of standard containing 10 ug/L each of As(III), As(V), MMA, DMA, and AsB.

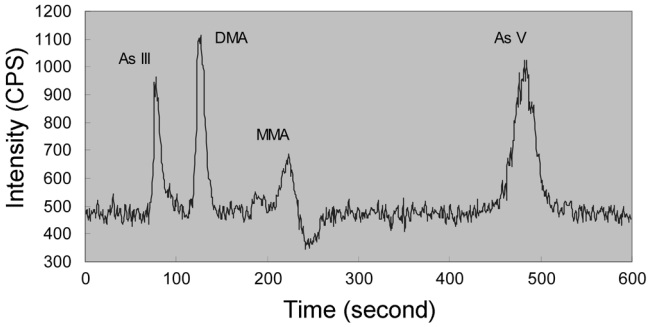

Figure 2. HPLC-ICP-MS chromatogram of arsenic species in a freeze-dried apple sample.

The results (Table 1) showed that enzyme extraction might be suitable for rice flour and freeze-dried apple, but it was not efficient for spinach. For spinach, extraction with TFA was the best. Other researchers have reported results after treatment with other enzymes such as trypsin.[34,37]

Separation and quantitation of arsenic species. A typical chromatogram of a standard containing a mixture of arsenic species (10 µg L^{-1} As(III), As(V), MMA, DMA, AsB) is shown in Figure 1.

Chromatogram of arsenic species from freeze-dried apple extracted by enzyme extraction is shown in Figure 2. The major arsenic species were As(III), As(V), MMA, and DMA. The arsenic species were quantified and summarized in Table 2. The mathematical sum of the four arsenic species found agreed with the total arsenic value obtained by microwave digestion and ICP-MS. B'Hymer and Caruso[8] found As(III), DMA, and As(V), but not MMA in this sample. The chromatographic recovery of arsenic was 99% which is comparable to the results (83-96%) obtained by B'Hymer and Caruso.[8]

Inorganic arsenic species were found in the freeze-dried apple sample. The source of inorganic arsenic is not known but could possibly be from past pesticide use. Several varieties of fresh apples purchased from local grocery stores (Fairfax, VA, USA) were freeze-dried and analyzed but no significant arsenic species were found.

The chromatogram for enzyme extracted rice flour is shown in Figure 3. The major species were DMA, MMA

Table 2. Arsenic Speciation Analysis of freeze-dried apple and rice flour with enzyme extraction

Sample	DMA	MMA	As(V)	As(III)	Sum of arsenic species found
Freeze-dried apple	18 μg kg^{-1}	7 μg kg^{-1}	36 μg kg^{-1}	19 μg kg^{-1}	80 μg kg^{-1} (99 % of total As:81 μg kg^{-1})
Rice Flour (NIST SRM 1568a)	116 μg kg^{-1}	10 μg kg^{-1}	58 μg kg^{-1}	–	184 μg kg^{-1} (72 % of total As:256 μg kg^{-1})

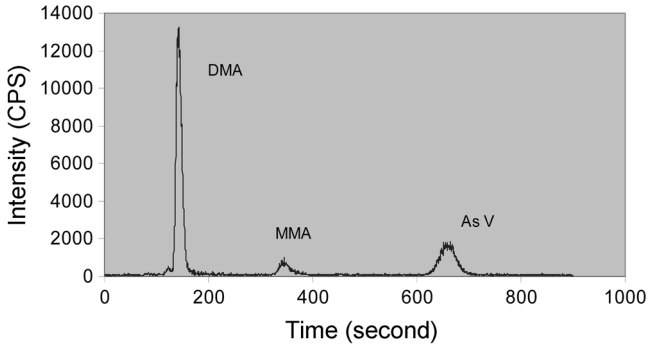

Figure 3. HPLC-ICP-MS chromatogram of arsenic species in rice flour SRM 1568a.

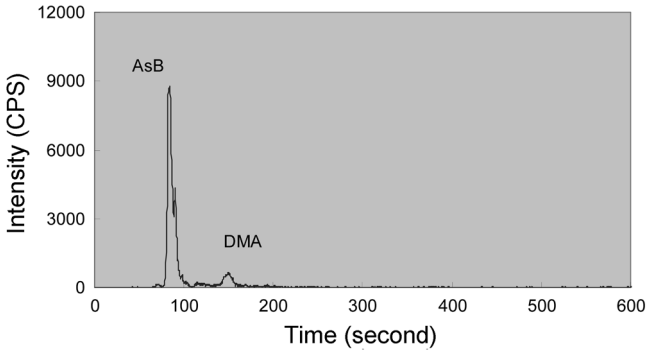

Figure 4. HPLC-ICP-MS chromatogram of arsenic species in tuna fish tissue BCR-627.

and As(V). Heitkemper *et al*. also found these species using amylase/50% methanol extraction.[11] Results are summarized in Table 2. The sum of the three arsenic species found was less than the total arsenic value obtained by microwave digestion and ICP-MS. Other researchers found inorganic arsenic in most or all rice samples examined in recent surveys.[28,35,36]

A shift in retention time occurred while analyzing the TFA extract from spinach when compared to the water based standards. During typical sample runs, the shift was large enough to prevent peak identification by retention time. The method of standard additions or standards made in TFA would probably be helpful. More research is required to investigate the cause of this shift.

Marine samples make up the majority of reference materials (RM) certified for arsenic species. Tuna fish tissue RM (BRC-627) was analyzed to evaluate our system. Many researchers have obtained good results using 50/50 MeOH/water mix.[7,38] Therefore, this mixture was chosen for extraction without evaluating other solvent mixtures. The major arsenic species found were arsenobetaine and DMA. The measured value for AsB (10.1 mg kg^{-1}) compared well with the certified value (9.3 mg kg^{-1}). However, the measured value for DMA (0.7 mg kg^{-1}) was considerably greater that the certified value (0.3 mg kg^{-1}). The results are summarized in Table 3 and the chromatogram is shown in Figure 4.

The enzyme extraction method was applied to dietary supplements. Mean total arsenic extraction efficiency was

Table 3. Arsenic Speciation Analysis of tuna fish tissue BCR-627 extracted with 50/50 MeOH/water

	Certified value (mg kg^{-1})	Measured value (mg kg^{-1})
Arsenobetaine	9.3	10.1
Dimethylarsenic acid	0.3	0.7

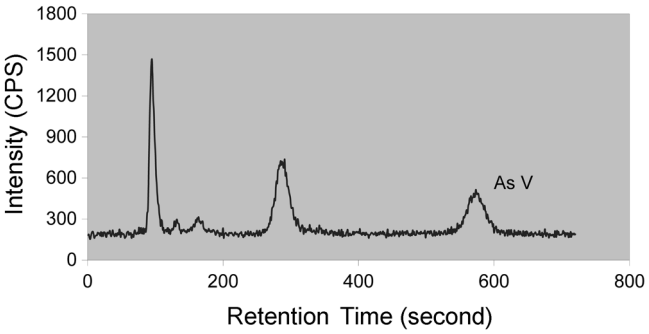

Figure 5. HPLC-ICP-MS chromatogram of arsenic species in an herbal dietary supplement (sample 3) with enzyme extraction.

68%. A Chromatogram of sample #1 (mixed herbal extracts) is shown in Figure 5. Three major peaks were present including one matching As(V) (200 µg kg^{-1}). The other two peaks were not identified. The unknown peaks were first thought to be from MMA and DMA with retention times shifted due to matrix effects. However, when arsenic species were spiked into the extract, the retention times of the unknown peaks did not correspond to any of the five species. A complementary experiment by electrospray mass spectrometry might help identify the unknown species. Total arsenic determined by microwave digestion and ICP-MS was 941 µg kg^{-1}. Thus, inorganic As(V) represented 21% of the total arsenic.

Chromatogram from a mixed ginseng supplement (sample #2) is shown in Figure 6. Three peaks were present: As(V) (450 µg kg^{-1}), MMA (150 µg kg^{-1}) and a small unidentified early peak. Total arsenic content was 750 µg kg^{-1} (determined by microwave digestion and ICP-MS). The combined As(V) and MMA species concentration was 510 µg kg^{-1}, 68% of the total arsenic.

Chromatogram from sample #3 (mixed herbal) is shown in Figure 7. Although several peaks were present, only

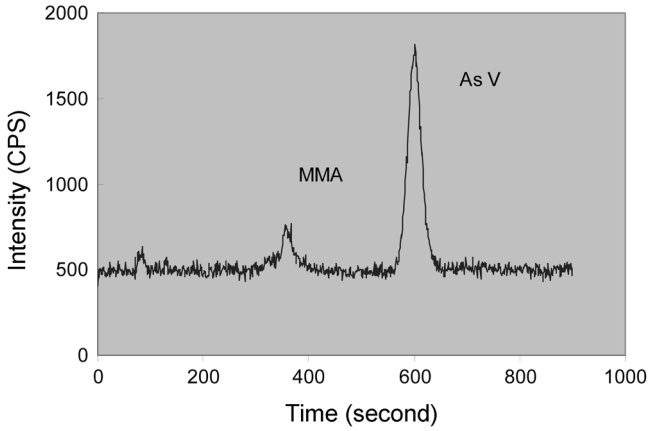

Figure 6. HPLC-ICP-MS chromatogram of arsenic species in an herbal dietary supplement (sample 2) with enzyme extraction.

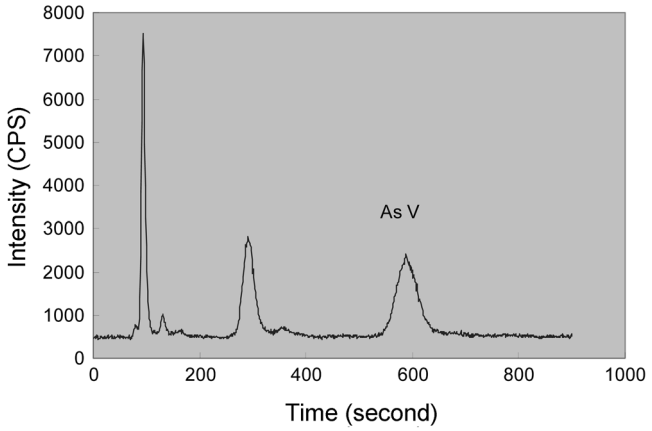

Figure 7. HPLC-ICP-MS chromatogram of arsenic species in an herbal dietary supplement (sample 3) with enzyme extraction.

As(V) (800 μg kg^{-1}) was identified. The total As content was 4200 μg kg^{-1}. The percentage of arsenic in inorganic form, as As(V), was 19%.

In this study, we realized the identification of arsenic species by retention time was not sufficient for dietary supplement samples because of the limited number of standards used. There was no evidence of matrix induced time shift of the inorganic arsenic peaks so a more comprehensive suit of organoarsenic compounds will be used in the future. Use of liquid chromatography-electrospray mass spectrometry will also help identify the unknown arsenic species.

Conclusions

This preliminary study of extraction methods for arsenic species analysis in food and dietary supplements indicates that the selection of extraction conditions will vary depending on the sample. ASE did not perform acceptably as an arsenic extraction method. More research is planned to investigate why ASE did not work well. Methanol extraction worked well for tuna. Enzymatic extraction with α-amylase was suitable for rice flour and freeze-dried apple, marginally effective for herbal supplements (68% extraction efficiency) but not effective for spinach. Its usefulness for use with herbal dietary supplements will have to be determined. Other enzymes such as trypsin or perhaps a combination of enzymes might be more universally applicable to herbal supplements. TFA extraction provided the best extraction efficiency for spinach and worked well for rice flour and dried apple. Therefore, TFA will be investigated further for use with herbal dietary supplements. A shift in retention time over the course of an analytical run was observed when TFA was used. Even though there might be some conversion of As(V) to As(III), TFA could still be useful in assessing inorganic arsenic and various organic species. Because of variable results mentioned above, the extraction efficiency of a method should be determined before proceeding to attempt quantitation of various As species that might be present. This is especially true for herbal dietary supplements because of the wide variety of supplements on the market. Inorganic arsenic in the form of As(V) was present in all three herbal dietary supplements. In two of the supplements, As(V) was a major fraction of the total arsenic. There also were several unidentified peaks in the chromatograms of the herbal supplements. A set of standards that included As(III), As(V), MMA, DMA and AsB was inadequate to identify all arsenic species in the herbal supplements. Future analyses of supplements must include a more complete set of standards in order to identify all organoarsenic compounds. A more extensive survey is planned to determine the following: the presence of inorganic arsenic in herbal supplements and the identity of all the organic species.

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