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Speciation analysis of arsenic compounds in edible oil by ion chromatography–inductively coupled plasma mass spectrometry

Yun-Ling Chu, Shiuh-Jen Jiang*

Department of Chemistry, National Sun Yat-Sen University, 70, Lien-Hai Road, Kaohsiung 80424, Taiwan

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ABSTRACT

An inductively coupled plasma mass spectrometer (ICP-MS) was used as an ion chromatographic (IC) detector for the speciation analysis of arsenic in edible oil. The arsenic species studied include arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine and arsenocholine. Gradient elution using $(NH_4)_2CO_3$ and methanol at pH 8.5 allowed the chromatographic separation of all species in less than 8 min. Effluents from the IC column were delivered to the nebulizer of ICP-MS for the determination of arsenic. The concentrations of arsenic species have been determined in several used and fresh vegetable oil samples. In this study, a microwave-assisted extraction method was used for the extraction of arsenic species from oil samples. The extraction efficiency was better than 92% and the recoveries from spiked samples were in the range of 90–105%. The precision between sample replicates was better than 8% for all determinations. The limits of detection were in the range of 0.008–0.024 ng mL^{-1} for various arsenic species based on peak height, which corresponded to 0.08–0.24 ng g^{-1} in the original oil sample. The major arsenic species in the used oil samples varied based on the food items cooked.

1. Introduction

The determination of trace elements in vegetable oils is one of the criteria for the assessment of the quality regarding freshness and storable period. Traces of heavy metals in vegetable oils are known to affect the rate of oxidation. Moreover, some of the metals are the subjects of food legislation [1,2]. According to the regulations of Taiwan government, the maximum allowed concentration of As in edible oil is 0.1 μg g^{-1}. Hence, determination of traces of arsenic in edible oils is important.

As reported in our previous paper [3], the concentration of arsenic in the oil might increase during cooking, especially when used for frying, due to leaching of arsenic from food stuffs cooked and repeated usage of same oil. However, not only the total concentration of arsenic, but also the concentration of individual species of arsenic is of great concern due to their varying toxicity. Several methods based on high performance liquid chromatography (HPLC), ion chromatography (IC) and capillary electrophoresis (CE) coupled with different detection methods have appeared in literature for arsenic speciation analysis in various samples [4–13]. However, only limited publications have been reported on the arsenic speciation analysis in edible oil samples [12]. In this study, an ICP-MS was employed as the ion chromatography detector for arsenic speciation analysis in edible oils.

The aim of the present work is to develop a simple and accurate method for the speciation analysis of arsenic in edible oil samples using IC–ICP-MS. The optimization of the IC–ICP-MS technique and its analytical feasibilities, and also its applications to the determination of arsenic compounds in edible oil samples, are described. Microwave-assisted digestion gained wide acceptance as a rapid method for sample decomposition for inorganic analysis. Recently, it has also been verified as an appropriate tool for rapid preparation of solid samples for organometallic speciation analysis [14–16]. In this study, microwave-assisted extraction method was used for the extraction of arsenic compounds in several used vegetable oil samples.

2. Experimental

2.1. Equipment and operating conditions

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

* Corresponding author. Tel.: +886 7 5252000x3929; fax: +886 7 5253908.
E-mail address: sjjiang@faculty.nsysu.edu.tw (S.-J. Jiang).

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Table 1
Equipment and operating conditions.

ICP-MS instrument	Perkin-Elmer SCIEX ELAN 6100 DRC II
ICP parameter	
RF power	1100 W
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.325 L min^{-1}
Nebulizer gas flow rate	0.90 L min^{-1}
Mass spectrometer settings	
Resolution	0.7 amu at 10% peak maximum
Dwell time	50 ms
Scan mode	Peak hopping
Sweeps/reading	3
Readings/replicate	2000
Replicates	1
Auto lens	On
isotopes monitored	m/z 75 (As), m/z 77 ($^{40}Ar^{37}Cl$ and ^{77}Se)
HPLC system	
Pump	Hitachi model L-6000 Hitachi model L-6100 (Intelligent pump)
Injector	Rheodyne 7125
Stationary phase	Hamilton PRP-X100 anion exchange column 10 μm particle diameter 4.1 mm i.d. × 250 mm length
Mobile phase	A: 0.5 mmol L^{-1} $(NH_4)_2CO_3$, 1% v/v methanol (pH 8.5) B: 50 mmol L^{-1} $(NH_4)_2CO_3$, 1% v/v methanol (pH 8.5)
Gradient program	0–0.1 min: 100% A; 0.1–7 min: 100% B
Mobile phase flow rate	1.0 mL min^{-1}
Sample loop volume	100 μL

Two HPLC pumps (Hitachi, Model L-6000 & L-6100), an injector (Rheodyne 7125) and an ion exchange column (Hamilton PRP-X100, 10 μm particle diameter, 4.1 mm i.d. × 250 mm length) comprised the IC system. Samples were loaded with a syringe onto a 100 μL sample loop. All separations were performed at room temperature. Each separation was attempted under different combinations of type and concentration of electrolyte, pH of mobile phase, method of gradient elution, etc. The conditions listed in Table 1 were those that yielded the best chromatogram of the various sets tested. The column outlet was connected to the pneumatic nebulizer of the ICP-MS device through polytetrafluoroethylene (PTFE) tubing (0.26 mm i.d. × 470 mm length).

2.2. Chemicals

Analytical-reagent grade chemicals were used without further purification. Purified water (18.2 MΩ-cm), from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used to prepare all the solutions. Dimethylarsinic acid, sodium arsenite(III) and ammonium carbonate were obtained from Sigma (St. Louis, MO, USA). Methanol, As(V) standard solution and Suprapur nitric acid (65%) were purchased from Merck (Darmstadt, Germany). Arsenobetaine (AsB) was obtained from BCR (Brussels, Belgium) as a solution of AsB in water (BCR CRM 626, 1031 ± 6 mg kg^{-1}). Arsenocholine was obtained from Argus Chemicals (Vernio, Italy). Disodium methyl arsenate was from ChemService (West Chester, USA). Stock solutions (1000 μg mL^{-1}) of all the arsenic species were prepared in pure water and diluted appropriately before use. The Ar gas used was provided by Hsin E Li Gases Co., Ltd. (Kaohsiung, Taiwan).

2.3. Sample preparation and extraction

The applicability of the developed procedure on the real samples was carried out on several used and fresh soybean oils. A microwave-assisted extraction procedure was used for the extraction of arsenic species from oil samples. A CEM MARS (CEM, Matthews, NC, USA) microwave digester was used in this study. Oil samples (0.500 g each) were weighed into 15 mL polyethylene centrifuge tubes and 10 mL of 0.5% v/v HNO_3 in 80% v/v methanol was added. The oil phase was at the lower layer of the liquid mixture. The tubes were then put into a beaker and exposed to microwave heating. The microwave system was programmed to maintain the temperature at 80 °C for 120 min. After microwave heating, the solutions were allowed to cool and directly centrifuged at 0 °C for 10 min at 4000 × g (MIKRO 22R, Hettich, Germany). The supernatant was decanted and then dried at 70 °C by Rotary evaporator for 20 min to remove most of the methanol. The extracts were diluted to 5 mL with pure water and then injected into IC–ICP-MS for arsenic determination. The concentration of arsenic species was determined by external calibration method based on peak area. The recovery was determined by spiking 0.5 g of oil sample with 2.5 ng each of various arsenic standards and then extracted by HNO_3 in methanol solution.

Since there is no reference value for the oil samples, in order to check the extraction efficiency of arsenic, the total concentrations of arsenic in the samples were determined, after emulsification of oil samples, by pneumatic nebulization ICP-MS. A 0.4 g portion of oil sample was transferred to a 10 mL flask, 1 mL of 10% v/v Triton X-100 and a drop of antifoam were added, then various amounts of As(V) standard solution was spiked. The emulsified sample was shaken and diluted to the mark with pure water and analyzed by pneumatic nebulization ICP-MS with 2 ng mL^{-1} of Ge as the internal standard [17]. The total concentrations of arsenic in the extracts were also determined by pneumatic nebulization ICP-MS with standard addition method. These results were compared with that obtained by IC–ICP-MS method.

3. Results and discussion

The efficiency of extraction of the arsenic species and their separation by IC involve optimization of several parameters. The detection of arsenic (m/z 75) with quadrupole-based ICP-MS can be problematic due to the isobaric interference of $^{40}Ar^{35}Cl^+$ if chlorides ions are present in the sample solution. If $^{40}Ar^{35}Cl^+$ is present, $^{40}Ar^{37}Cl^+$ also needs to be present as Cl has two isotopes having masses 35 and 37. Hence, to ascertain the presence of $^{40}Ar^{35}Cl^+$, signal at m/z 77 was monitored. From the experiment it was found that no appreciable signal was obtained at m/z 77 indicating that the signal at m/z 75 was attributed to arsenic ions only. The following are the observations of optimization parameters.

3.1. Selection of ion chromatography operating conditions

As reported in a previous paper, five arsenic compounds, namely As(III), As(V), MMA, DMA and AsB were separated by using ion exchange column with $(NH_4)_2CO_3$ as mobile phase [5]. Preliminary studies were carried out using the conditions similar to the previous work. A gradient elution using 0.5 mmol L^{-1} and 50 mmol L^{-1} $(NH_4)_2CO_3$ was carried out and the gradient program was, 100% 0.5 mmol L^{-1} $(NH_4)_2CO_3$ from 0 to 0.5 min, 100% 50 mmol L^{-1} $(NH_4)_2CO_3$ from 0.5 to 9 min and 100% 0.5 mmol L^{-1} $(NH_4)_2CO_3$ from 9 min till completion of the experiment. Fig. 1 shows the effect of the pH of mobile phases on the chromatogram. From the experimental results it was found that AsB and As(III) could not be separated when the pH was less than 8.0, in contrast, AsC and AsB, As(III) and DMA, MMA and As(V) could not be separated when the pH was higher than 9.0. For better separation of various arsenic compounds, pH 8.5 was selected for the following experiments. Effect of the concentration of $(NH_4)_2CO_3$ in mobile phase A on the chromatogram was studied using 0.1, 0.5

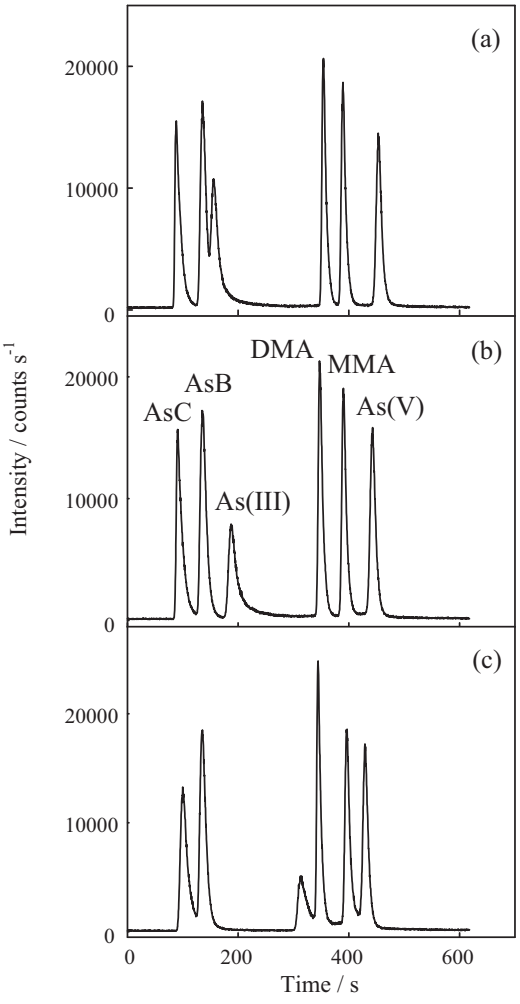

Fig. 1. Effect of the pH of mobile phase on chromatogram; (a) 8.0, (b) 8.5, and (c) 9.0. Mobile phase A contained 0.5 mmol L^{-1} $(NH_4)_2CO_3$ and 1% methanol and mobile phase B contained 50 mmol L^{-1} $(NH_4)_2CO_3$ and 1% methanol. The injected solution contained 5 ng As mL^{-1} of each of the arsenic species studied. The other conditions are given in Table 1.

and 1 mmol L^{-1} of the $(NH_4)_2CO_3$. It was found that the concentration of $(NH_4)_2CO_3$ in mobile phase A did not affect the separation significantly. 0.5 mmol L^{-1} $(NH_4)_2CO_3$ was selected for following experiments. Although not shown in the text, the effects of the concentration of methanol in mobile phase A and B [18,19], the mobile phase flow rate and the programming of gradient elution, etc., have also been studied to achieve better chromatogram. The conditions listed in Table 1 are those that yielded the best chromatogram of the various sets tested. A typical chromatogram of a solution containing 5 ng mL^{-1} (as element) of As(III), As(V), MMA, DMA, AsB and AsC is shown in Fig. 2. As shown, all the six species studied were well separated in less than 8 min. However AsC was eluted closely with the solvent peak. At the optimized conditions, the following parameters have been computed. Repeatability was determined using five consecutive injections of a test mixture containing 5 ng mL^{-1} each of the six arsenic species studied. The relative standard deviation of the peak areas was less than 7% and the repeatability of retention time was better than 1% for all species. Calibration curves (five points) based on peak heights and peak areas were linear with correlation coefficient (r) better than 0.9997 for each species in the range studied (0.1–10 ng mL^{-1}). From the experimental results, we found that the calibration sensitivities of various arsenic species based on peak area are similar.

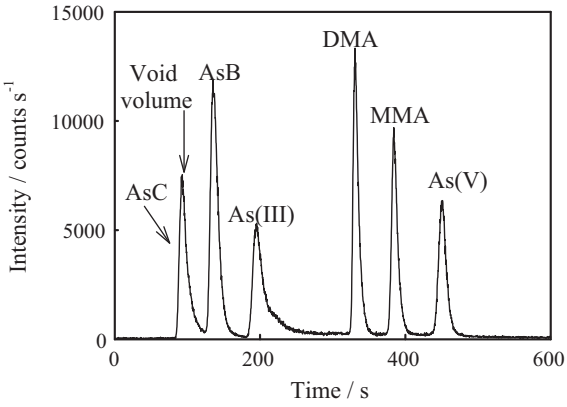

Fig. 2. Typical element-selective chromatogram for AsC, AsB, As(III), DMA, MMA and As(V). Each arsenic species was present at 5 ng mL^{-1} (as element). IC conditions are given in Table 1.

The detection limit was estimated from the peak height versus concentration plot and based on the concentration (as element) necessary to yield a net signal equal to three times the standard deviation of the background. The IC–ICP-MS detection limit was 0.015, 0.01, 0.024, 0.008, 0.01 and 0.013 ng mL^{-1} for AsC, AsB, As(III), DMA, MMA and As(V), respectively. The detection limits of various arsenic species obtained in this work were better than or comparable to previous results with similar techniques [6–10,20,21].

3.2. Determination of total concentration of arsenic in oil samples

In order to prove that the system is suitable for practical analysis, three used soybean oils (Oil #1, Oil #2, Oil #3) and one fresh oil (unused form of Oil #2) were analyzed. Since there is no reference value for the real-world samples, in order to check the total extraction efficiency of arsenic, we need to compare the total arsenic concentrations in the extracts and in the original samples using the present procedure. Since the oil samples could produce a lot of vapor during decomposition, it is not an easy task to dissolve the oil sample completely. Hence the arsenic concentration in the oil was quantified by means of standard addition method with 2 ng mL^{-1} of Ge as the internal standard using the procedure described in Section 2. The total concentrations of arsenic in oils are listed in Table 2. The total concentration of As in the fresh sample of Oil #2 was below the method detection limit (<0.15 ng mL^{-1}) and hence could not be determined. However, it is interesting to note that the concentration of As was elevated in the used sample of Oil #2. Thus, arsenic might have been leached from the food stuffs during cooking and resulted in increased concentration.

3.3. Extraction of arsenic from edible oil

In this study various solutions, namely deionized water, 50% v/v methanol, 80% v/v methanol and 2% v/v Triton X-100 were tested as the extracting solution for the extraction of total arsenic from a used soybean oil (Oil #1) at the extraction temperature of 60 °C for 30 min by microwave heating. From the experiments it was found that better extraction efficiency could be obtained when 80% v/v methanol was used as the extracting solution. The effect of the extraction time on extraction efficiency was studied at 30, 60, 90 and 120 min. It was found that the extraction efficiency increased with the increase of extracting time; 120 min was selected. The effect of the extraction temperature on extraction efficiency was also studied. It was found that the efficiency increased

Table 2
Concentrations and recoveries of arsenic compounds in oil as measured by IC–ICP-MS[a] ($n = 3$).

Compound	Oil #1		Oil #2		Oil #3	
	Conc. found/ng g^{-1}	Recovery[b]/%	Conc. found/ng g^{-1}	Recovery[b]/%	Conc. found/ng g^{-1}	Recovery[b]/%
AsC + unknown?	1.51 ± 0.02	105 ± 1	7.75 ± 0.13	99 ± 5	2.71 ± 0.11	98 ± 2
AsB	0.95 ± 0.07	94 ± 3	3.18 ± 0.21	100 ± 5	0.51 ± 0.02	101 ± 4
As(III)	2.60 ± 0.02	90 ± 2	1.62 ± 0.11	99 ± 7	1.63 ± 0.07	95 ± 5
DMA	2.17 ± 0.06	95 ± 3	1.77 ± 0.03	102 ± 4	0.21 ± 0.01	100 ± 4
MMA	2.17 ± 0.06	96 ± 4	1.32 ± 0.10	100 ± 3	0.19 ± 0.01	93 ± 3
As(V)	10.5 ± 0.22	101 ± 2	0.94 ± 0.06	102 ± 3	1.44 ± 0.09	101 ± 1
Sum of species[c]	19.9 ± 0.25(97%)		16.6 ± 0.29(95%)		6.69 ± 0.16(101%)	
Extract[d]	20.5 ± 0.9(92%)		17.5 ± 0.8(96%)		6.61 ± 0.21(94%)	
Total[e]	22.4 ± 1.7		18.3 ± 1.1		7.01 ± 0.20	

[a] Values are means of three measurements ± standard deviation.
[b] Recovery was determined by spiking the 0.5 g of oil sample with 2.5 ng of As species standard.
[c] The value shown in parenthesis is the percentage of the sum of the species to the total extracted concentration.
[d] The value shown in parenthesis is the percentage of the total arsenic in the extract to the total arsenic concentration in oil.
[e] Determination by pneumatic nebulization ICP-MS with standard addition method after oil was emulsified.

with the temperature. An extraction temperature of 80 °C was selected for the following experiments. The total concentrations of arsenic in the extracts were determined by pneumatic nebulization ICP-MS with standard addition method. From the experiment it was found that only about 50% of the total arsenic was extracted under the conditions selected. According to the paper reported by Foster et al. [22], the addition of HNO_3 in the extraction solution could help the extraction of arsenic from marine plant and animal tissues. In this study, a mild condition of 0.5% v/v HNO_3 in 80% methanol was tested as the extraction solution. From the experiment it was found that the extraction efficiency of arsenic from oil emulsion improved significantly. To achieve better extraction efficiency, after evaluation, a microwave-assisted extraction of As species from oils using 0.5% v/v HNO_3 in 80% methanol at 80 °C for 120 min was selected for the following analyses. As shown in Table 2, the extraction efficiency was better than 92% for all determinations.

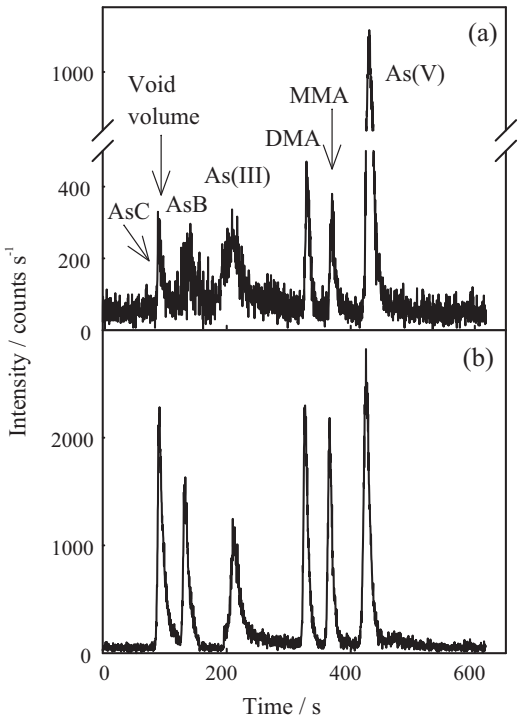

Fig. 3. Typical chromatogram of (a) the extract of Oil #1 and (b) Oil #1 spiked with 5 ng g^{-1} each of arsenic standards. The concentrations of AsC and As(V) in injected solution were 0.14 and 1.05 ng mL^{-1}, respectively.

3.4. Arsenic speciation analysis in oil samples

In order to prove that the system is suitable for practical analysis, three used oil samples (Oil #1, Oil #2, Oil #3) were analyzed for arsenic compounds. The extraction of arsenic species of interest in used oil samples has been carried out by using 0.5% v/v HNO_3 in 80%

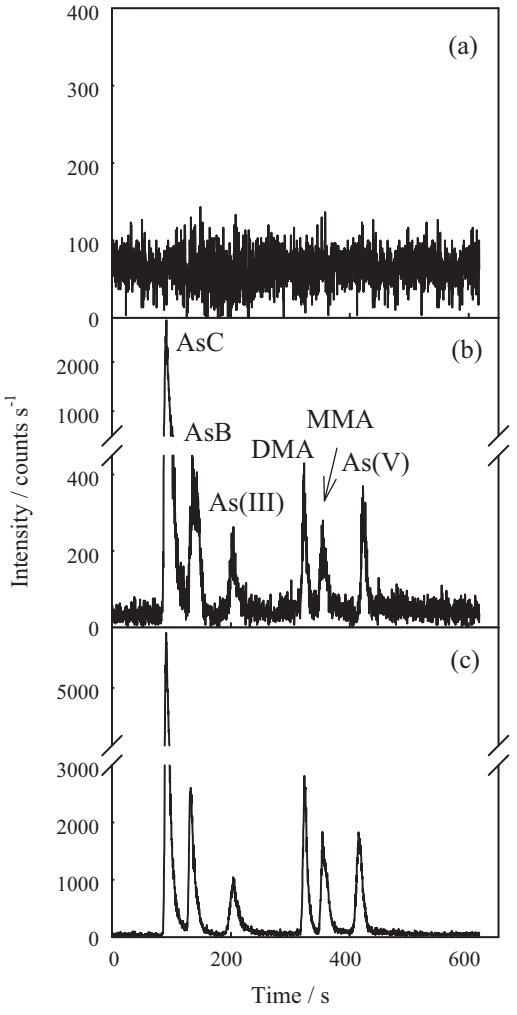

Fig. 4. Typical chromatogram of (a) the extract of unused form of Oil #2, (b) the extract of Oil #2, and (c) Oil #2 spiked with 5 ng g^{-1} each of arsenic standards. The concentrations of AsC and As(V) in injected solution were 0.78 and 0.09 ng mL^{-1}, respectively.

v/v methanol at 80 °C. A 100-μL injection of the extract of edible oil was analyzed for As species using the IC–ICP-MS method. The typical chromatogram for Oil #1 and Oil #2 recorded at m/z 75 is shown in Figs. 3 and 4, respectively. Various arsenic species studied in this work were present in the used oil samples (Figs. 3 and 4). As shown in Fig. 4(a), no arsenic compound was detected in the unused form of Oil #2; the results demonstrated that the arsenic compounds in used oil were leached from the foods cooked. As shown, As(V) was the major species in Oil #1 and AsC and AsB were the major arsenic species in Oil #2. However the peak area of AsC in Oil #2 was larger than expected. It could be due to the co-elution of unknown arsenic compounds (possibly arsenosugars [13,23]) with AsC, which needs further identification using ESI-MS/MS. Oil #2 was collected from a seafood restaurant, while the Oil #1 and Oil #3 were collected from the Chinese Style Fried Chicken booths where much more diverse food stuffs (chicken, seafood, vegetable, etc.) were fried. From the experiments it was found that the major arsenic compounds in the used oils varied possibly due to the change the food items cooked. Furthermore the organic arsenic compounds are quite stable even under a high temperature cooking conditions. In this study the peak areas of the elution peaks were used for the quantitative evaluations. The recoveries listed in Table 2 are determined by spiking the oil samples with arsenic species studied, each of 5 ng g^{-1}, and then extracted by HNO_3 in methanol solution as described above. As shown, recoveries were in the range of 90–105% for the species studied in different samples. The amounts of As present in these oil samples were quantified by an external calibration method, the results are listed in Table 2. Since the calibration sensitivities of various arsenic species based on peak area were similar, the concentration of unknown, if present, was estimated against the sensitivity of AsC. As shown, the IC–ICP-MS results were compared with the total concentrations of As in these oil samples quantified after emulsification and found to be in satisfactory agreement with the total concentrations. The precision between sample replicates, of different experiments including extraction, separation and determination ($n = 3$), was better than 8% for all determinations. The concentration of As in the analyzed oil samples is far below the maximum allowable concentration 0.1 μg g^{-1}.

4. Conclusion

Speciation of arsenic in edible oils can be carried out by IC–ICP-MS. All the six species studied were well separated in less than 8 min. The arsenic species in oil samples were extracted into 0.5% v/v HNO_3 in 80% v/v methanol solution using microwave heating. Under these conditions, more than 92% of the total arsenic in oil samples was extracted. The concentration of arsenic species in used oil was higher than the unused oil due to the leaching of arsenic from the food stuffs fried for longer periods. It is possible that some unknown arsenic species are present in the sample whose identity and quantification can be carried out using appropriate arsenic standards and ESI-MS/MS, especially, in Oil #2.

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