International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2018): 7.426

Total Arsenic and Arsenic Species in Environmental Samples

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Abstract: ***A variety of extraction procedures methanol-water (1:1, 9:1, 1:1-9:1),enzymatic extractionand phosphoric acid were evaluated for the extraction of arsenic species in rice, quinoa, carrots, beet and soil samples and final determination by HPLC-ICP-MS has been developed. Presence of arsenite (As(III)), arsenate (As(V)), monomethylarsonicacid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB) and unknown peak were detected and quantified using anionic Hamilton PRPX-100 column at pH 6 and phosphate mobile phase 10mM. Extraction efficiencies of the different extracting solutions were evaluated by comparing the total Ascontent in the extractafter the mineralization and final determination by HG-AFS.***

Keywords: Arsenic species extraction, environmental samples

1. Introduction

Quantitative and reproducible extraction of species, especially from solid samples is the weakest link in the sequence of analytical operations. For elemental compounds analysis, solid samples require certain form of sample pre-treatment prior determination. The common pre-treatment techniques include solvent extraction todeterminearsenic species in biological samples with several solvent systems [1].

The extraction recoveries vary with types of sample, extraction time, solvents and extraction temperature, the alternative extraction procedure is essential. The mixture methanol-water at different ratio is the most widely used nowadays and combination of two or more separation methods must be applied for speciation of organic and inorganic As species[2]. Among these, most commonly analyzed, because of their importance in environmental analysis are As(III), As(V), MMA, DMA, AsB, AsC. However, the extraction recovery depends of each matrix.

The extraction of arsenic species from environmental samples is a very complex mater[3]. In which two conflicting issues have to be balanced: obtaining an adequate recovery, on the one hand, and preventing losses especially destruction of the species. The quality control of analytical measurements implies that the extraction recoveries are verified which can be done in several ways. For extraction losses e.g. degradation or incomplete recovery of compound, it is current practice to apply compensation for these losses by connecting the results with a recovery factor[4] in order to achieve a better approximation to the true value in material. These correction factors are established after undertaking recovery studies which are an essential component of the validation of extraction based techniques. To obtain this recovery factors are not easy fast since it depends of each matrix and for different levels of contents. In the case where the total contents of compounds have to be measured corrections for recoveries should, in principle, be applied and if the extraction is only partial, the results have to be related to the actual extraction method use and referred to as extractable contents; the comparability of results will only be achievable, in this instance[5]. Finally the corrected values can be scarcely comparable if recoveries are calculated in different ways. An analytical methods for arsenic speciation in samples based on the use consecutive extractions with the mixture 1:1, 9:1, 1:1-9:1 methanol : water, water and phosphoric acid 1M[6] are proposed to separate and quantify the As species by anionic chromatography coupled to the ICP-MS.

This article discusses the evaluation of consecutive extraction recoveries of arsenic species in samples extracts of rice, quinoa, carrots, beet and soil.

Arsenic is generally considered to be a toxic element, and so undesirable in food. Onespeciesof arsenic of arsenic, arsenobetaine is however found at high concentration in marine fish[7] fortunately this form of the element iscompleted harmless. Rice[8, 9] is a food in various part of the world it acts as a bio-accumulator for arsenic. The importance or arsenic level insoil [6, 10] has considerable effects on the use of land for housing, agriculture and so.

2. Literature Survey

The analysis of trace elements in biological sample such as plants and animals and environmental samples such as air, water and soil can give as an indication of the amount of pollution and contamination in the environment. It is important to monitor the elements that enter into the environment because many of them are toxic and may have adverse effects on plants and animals and eventually enter into the human food chain.

Many elements are of environmental concern due their know toxicity. Of current concern are the effects they have on marine life[11]. The toxicity of arsenic is highly dependent upon its chemical form [12]. Of the inorganic forms, arsine is highly toxic, and arsenite is accepted as being more toxic than arsenate[13].The methylated organic species monomethylarsonic acid and dimethylarsonic acid are less toxic than the inorganic forms, and organoarsenicals arsenobetaine and arsenocholine are generally considered nontoxic[14]. Arsenic may enter into the environment from agricultural uses such as pesticides and fertilizers, or industrial uses such as the production of alloys and

glass[15]. The presence of arsenic in fish, shellfish and crustaceans has been known for many years [16].

3. Methods

3.1 Instrumentation

For the determination of total arsenic concentration a flow injection hydride generation atomic fluorescence spectrometer , FI-HG-AFS (Excalibur , PSA,UK) was used Polytetrafluoroethylene tubing (id 1.6 mm) was used in all connections.

An inductively coupled plasma mass spectrometry, HP ICP-MS operating under normal multielement tuning conditions was used as detection after HPLC species separation.

The column effluent was directly introduced into a Babington glass nebulizer and a double pass Scott type spray chamber with surrounding water jacket hold at 5°C. Single ion monitoring at m/z 75 was used to collect the data. All signals quantification was made in the peak area mode. The peaks were integrated using the ICP-MS software.

For chromatographic separations, a high pressure model Milton Roy pump (LDC Division, Rivera Beach, Florida USA) was used as sample delivery system. The injection valve was model 9125 Rheodyne (USA). All the connections were made of polytetrafluoroethylene tubing (id 0.5 mm). The ion exchange columns and chromatographic conditions were used for species separation and quantification. The analytical parametersof FI-HG-AFS, ICP-MS and HPLC are in Table 1.

Sample mineralization and species extraction were carried out furnace digestion system (Reactor Savillex Corporation 6138, Mineuka USA in an oven. An I.R. distiller (Berghof, BSB-9391 R) was used for HNO_3 and HCl purification.

The supernatants were evaporated using a Centrivap Evaporator and Cold Trap system (Labconco, Kansas City, MO USA). Sonication of samples was performed in a focused ultrasonic bath (Bandelin Sonopuls HD-2200, Fungilab S.A. US).

3.2. Materials and reagents

Stock solutions of 100 µg/mL arsenic as MMA, DMA, As(III), AsB and As(V) were made and diluted to appropriate volume with deionized water (Milli-Q Ultrapure water system, Millipore, USA) before analysis. Standard solutions of 100 µg/mL arsenic as $CH_3AsO_3Na_2$ (MMA), Merck 98%, arsenic as $C_2H_6AsNaO_2$ $X3H_2O$ (DMA), Fluka 98%, arsenic as inorganic arsenic as $NaAsO_2$, (As(III)) Sigma Aldrich, St. Quintin Fallavier, France 100%. Arsenic as $C_3H_6AsCH_2COOH$ (AsB), Tri Chemical Laboratory INC, Japan, 99% and Arsenic as $Na_2HAsO_4X7H_2O$, As(V) Sigma Aldrich, St. Quintin Fallavier, France 100%.

The stock solutions were kept at 4°C in the dark and the working solutions were daily prepared.

The extractant mixtures were prepared from deionized water and HPLC –grade methanol (Merck, Darmstadt, Germany). High purity nitric and hydrochloric acids were obtained by distillation of reagent grade (Merck). HF acid was Suprapur grade Merck. $K_2S_2O_8$ (Fluka 99.5%) were prepared in NaOH (Suprapur Merck). H_2SO_4 (Suprapur 96%, Merck) and $NaBH_4$ (Fluka 98%) in NaOH, used for reduction were prepared daily**.** The $NaBH_4$solution was filtered through a 0.45 µm cellulose acetate membrane. H_3PO_4 and $HClO_4$ were obtained from Merck.

The chromatography mobile phase was 10 Mm ammonium dihydrogen phosphate (Merck), adjusted to pH 6.0 with 0.1% NH_4OH (Fischer certified ACS grade) Mobile phase was filtered through a 0.45 µm nylon membrane.

3.3. Types of Samples

Arsenic compounds were determined in samples of environmental and biological origin: Quinoa, carrots, beetand soil samples were collected from the Chiu Chiu area (Chile). About 10 Kg of soils were taken randomly following the established protocol[17].They were taken at a depth of 5-7 cm, dried, sieved in the place to a grain size of 1.25 mm to obtain homogeneous sub-samples. Samples were sent to the laboratory in polycarbonate bags at ambient temperatures (20ºC). About 10 Kg of carrots (*daucus carota*), beets (*beta vulgaris*) and quinoa (chenopodium) were taken from the Chiu Chiu area. The samples were sent fresh from origin to laboratory maintained under N_2 gas. The edible rice sample studied was bought in Chilean Supermarkets. The rice was ground to a particle size of 500 microns, homogenized and bottled. This rice was not desiccated or lyophilized and its moisture content was about 1.5% after grinding.

Certified reference materials (CRMs)**:**Rice Flour (1568[a] NIST), Tomato Leaves (NIST 1573a) and Montana II Soil (NIST SRM 2711a) were used to validate the total arsenic determination and for total As species characterization and / or validation.

3.4. Procedures

3.4.1. Mineralization of total arsenic determination

3.4.2. Rice, quinoa, carrots and beet samples

About 0.5 g of sample was placed into a Teflon reactor, 10 mL of suprapur concentrated HNO_3 were added and the reactor were covered and pre-digested overnight. Next, 20 mg of $NA_2S_2O_8$and 3 mL of $HClO_4$ (or 0.3 mL of concentrated HF, if the silica content was high in the rice) was added and heated to 150°C for 3 hours in an oven.

After cooling, 0.5 mL of concentrated suprapur H_2SO_4 was added and the digested sample was heated by refluxing for about 2 hours until the final volume was about 2 mL. Then, sample was diluted to 10 mL with 0.5 M HCl. For analysis, three subsamples and blanks were prepared in parallel and each one was analyzed in triplicate.

3.4.3. Soil Sample

Approximately 0.5 g the sample was placed into the Teflon reactor and 10 mL the mixture 1:3 HNO_3: HCl and 0.5 mL HF were added. The mixture was maintained at150°C for 2 hours. After cooling the digested samples were heated until total elimination of the nitric acid, and finally diluted to 25 mL with 0.5 M HCl.

3.5. Extraction proceduresof arsenic species

3.5.1 Procedure 1: Methanol : WaterRice, quinoa, carrots and beet samples

Approximately 1.0 gof the fresh homogeneous mesh of edible part of vegetableswas placed in a Teflon reactor and 10 mL of 1:1 methanol: water mixture was added following a treatment similar to that performed by Shibata and Morita[18].The mixture was heated for 30 min, at 55ºC, sonicated with an ultrasonic probe for 5 min at 30% power and centrifuged at 5000 rpm for 20 min at ambient temperature. The procedure was repeated in the solid fraction. The two liquid extracts were pooled and evaporated to a final volume of 2 mL and filtered through a 0.45 µm Nylon syringe filter. The same procedure was followed for extraction in 9:1 methanol: water and 1:1 – 9:1 (1:1 followed by 9:1) mixtures. Each residue was dissolved in adequate water volumes, filtered (0.45 µm) and kept frozen (-20°C) prior to analysis. Three extracts were prepared from each sample and reference material.

3.5.2 Procedure 2: Enzymatic extraction: Rice, quinoa, carrots and beet samples

To 0.3 g of the fresh homogeneous mesh of edible part of vegetables, 10 mg alpha-amylase and 3 mL water was added. The mixture was sonicated with an ultrasonic probe for 60 s 30% power in a bath ice. After that, 30 mg protease was added, and the mixture was again sonicated with an ultrasonic probe for 120s at and centrifuged for 10 min at 4000 rpm. The solution was made up to 2 mL for analysis.

3.5.3 Procedure 3: Phosphoric Acid: Soil Sample

Approximately 0.3 g of the soil sample was placed in a Teflon reactor and 10 mLof 1M phosphoric acid were added. The mixture was heated at 150°C for 3 hours and the resultant extract evaporated to dryness. The residue was dissolved with 25 mL of 10 mM phosphate solution at pH 6. Three extracts were prepared from each sample. The procedures were performed in triplicate. Table 1 shows the chromatographic conditions for As species separation.

Table 1: Shows the optimized instrumental parameters for HG-AFS, ICP-MS and HPLC systems.

HG-AFS	
$NaBH_4$ concentration	1% w/v
HCl concentration	1.5 M
Flow rate of $NaBH_4$ and HCl	1.0 mL min^{-1}
Sample flow rate	0.8 mL min^{-1}
H_2 flow to feed diffusion flame	60 mL min^{-1}
Ar carrier gas flow	200 mL min^{-1}
Ar auxiliary gas flow	100 mL min^{-1}

ICP-MS	
R.F. power	Forward:1350 W Reflected: 2.2 W
Ar flow rate	Coolant: 14 L min^{-1} Nebuliser:1.0 L min^{-1} Auxiliary: 0.9 L min^{-1}
Measurement mode	Peak area of ^{75}As

HPLC

Column	Mobile phase	pH	Flow rate	Injection
PRP-X100	Phosphate/NH_3, *Gradient mode (%)* *A:5mM; B: 25mM* 0-15 min (A:100-0 and B:0-100) 15-25 min (A:0-100 and B:100-0)	6.0	1.5 mL min^{-1}	100µL

3.5. Total Arsenic determination

Total arsenic concentrations were determined in each raw material and extracts after their mineralization by flow injection – hydride generation – atomic fluorescence spectrometer. The operating parameters used are given in Table 1. The analytical signals were evaluated as peak height and quantification out by the standard addition method.

3.6. Determination of Arsenic species

The Arsenic species were separated by HPLC following a method similar to that proposed by Beauchemin[19], injecting 100 µL in the anion exchange column PRP- X100 and eluted isocratically using 10 mM phosphate at pH =6 as mobile phase,under the conditions given in Table 1. The Arsenic species were quantified by measurement of the peak area by ICP-MS. 10 μgL^{-1} of Ge was used as the internal standard to correct any drift in the response of the ICP-MS. Since the results achieved on the speciation by external calibration and standard additions matched well, it was no longer necessary to apply the standard addition. It has been demonstrated by monitoring both $^{40}Ar^{35}Cl$ and $^{40}Ar^{37}Cl$ (m/z 75 and 77) that the presence of chloride does not interfere because of its low concentration in all the extracts.

4. Results and Discussion

4.1. Extraction Efficiency of total Arsenic for rice, quinoa, carrots, beet and soil

In order to increase the extraction efficiency achieved, three consecutive extractions were carried out for each extractant tested: methanol-water (1:1, 9:1, 1:1-9:1),enzymatic extraction and 1 M H_3PO_4 only for soil samples.

Table 2 shows the total arsenic content found in rice, quinoa, carrots, beet and soil, after acid digestion of samples and determination by HG – AAS, and the percentage of total arsenic in each extract. The detection limit for total As was 5.0 ngg^{-1}.The total Arsenic in each extract was determined by HG – AAS after mineralization in similar conditions as those used for the raw sample. The extracts were conveniently digested to form species capable of generating arsine in the presence of borohydride.

Table 2: Extraction efficiency of total arsenic in rice, quinoa, carrots, beets and soil Expressed as percent x ± s for three consecutive extractions

Sample (Total content $mgKg^{-1}$)	Extraction efficiency % Number of extraction	Methanol – Water 1:1	Methanol – Water 9:1	Enzymatic 1.1-9:1	Enzymatic	$1M\ H_3PO_4$
Rice (0.183 ± 0.050)	1st	85.0 ± 3.1	65.2 ± 4.1	79.3 ± 2.6	20.3 ± 2.6	-
	2st	10.8 ± 1.8	15.2 ± 2.3	10.1 ±1.5	4.5 ± 1.5	-
Quinoa (0.290 ± 0.061)	**Σ Extractions n=3**	98.8 ± 4.0	87.4 ± 5.2	91.0 ± 2.6	28.8 ± 2.4	-
	1st	92.8 ± 3.0	62.4 ± 3.8	72.5 ± 3.3	11.9 ± 1.8	-
	2st					
Carrots (0.600 ± 0.049)	**Σ Extractions n=3**	5.2 ± 1.5	10.9 ± 1.6	9.1 ± 1.9	ND	-
	1st	100.0 ± 5.4	80.9 ± 3.5	89.7± 5.2	11.9 ± 1.8	-
	2st					
Beets (0.750 ± 0.044)	**Σ Extractions n=3**	82.8 ± 5.0	55.4 ± 4.2	72.8 ± 4.9	19.5 ± 2.5	-
	1st	9.2 ± 1.5	12.8 ± 1.1	11.3 ± 2.3	4.0 ± 1.9	-
	2st					
Soil (64.33 ± 1.00)	**Σ Extractions n=3**	98.5 ± 2.6	80.3 ± 3.7	94.8 ± 3.9	25.5± 3.1	-
	1st	ND	ND	ND	85.8 ± 4.9	-
	2st					
	Σ Extractions n=3	ND	ND	ND	8.1± 1.2	-
		ND	ND	ND	98.9± 5.1	-
		50.8 ± 2.7	35.8 ± 2.9	46.9 ± 4.0	ND	89.0 ± 4.5
		7.5 ± 1.1	6.2 ± 1.5	5.5 ± 1.9	ND	6.5 ± 1.6
		69.3 ± 3.9	47.6 ± 3.1	58.7 ± 3.5	ND	100.0 ± 9.5

The 9:1 methanol-water mixture for arsenic extraction from rice is not adequate, providing the worst recoveries (65.2% in the first extraction). Analogous results were obtained for 1:1 and 1:1-9:1 methanol: water extracts. About 85% of the total arsenic in rice was extracted in 1:1 methanol – water in the first run, which means that one extraction might be sufficient to identify and quantify the arsenic species present in this matrix. An almost quantitative recovery was achieved with three extractions from the 1:1 and 1:1 - 9:1 methanol: water mixtures. However, the 1:1 methanol – water mixture provided clearer extracts and the procedure was faster than that required for the 1:1-9:1 and the 1:1 methanol-water mixture was chosen as the most appropriate extractant, providing the highest extraction efficiency (98.5%) for the three consecutive extractions.The 1:1 methanol: water mixtures is appropriate for extraction of the total As species in carrots and quinoa, but not for beets, in which is necessary the enzymatic extraction.

It is important to mention that the efficiency of H_3PO_4 as an As extractant for soil is much higher than the different methanol: water mixtures. About 89% of the arsenic was recovered in only one extraction run. An almost quantitative recovery was achieved in two consecutive extractions steps, 95.5 and 100% within three consecutive extractions runs.

4.2. Arsenic species extraction for rice, quinoa, carrots, beet and soil

Six non - volatile species (arsenite, arsenate, MMA, DMA, AsC, AsB) were considered for arsenic by HPLC – ICPMS in these matrices.

We evaluated whether there any difference in the extraction efficiency between arsenic species for the different extractant checked. We also checked whether the second or third extraction could preferentially extract anyspecies not extracted in the first one.

Table 3: Efficiency of As species extraction in the samples analyzed. Expressed as percent X ± S referring of total content in the corresponding extract

Sample	Methanolic Extraction (1:1) Efficiency (%)	Enzymatic Extraction Efficiency (%)	$1M\ H_3PO_4$ Efficiency (%)
Rice	Total As :98.8 ± 4.0 As(III) 40.1±2.7 MMA12.5± 1.1 DMA 20.2± 2.1 As(V) 18.4± 2.9	Total As: 28.8 ± 2.4 As(III) 13.5± 3.2 MMA 4.3± 1.1 DMA 6.7± 1.0 As(V) 4.2± 1.1	-
Quinoa	Total As: 100.0±5.4 As(III)20.2± 3.3 As(V)78.5± 7.5	Total As: 11.9 ± 1.8 As(III): 10,9 ±1.5 As(V): n.d.	-
Carrots	Total As: 98.5 ± 2.6 As(III) 50.6± 9.0 As(V)46.3 ±5.0	Total As: 25.5± 3.1 As(III): 15.8± 2.3 As(V): n.d.	-
Beets	Total As: n.d. As(III) n.d. As(V) n.d.	Total As: 98.9± 5.1 As(V): 32.6± 4 Unknown: 65.1± 7	-
Soil	Total As: 69.3 ± 3.9 As(III) 9.1 ±2.3 AsB 14.4± 4.5 MMA10.3± 2.6 DMA 4.4± 1.3 As(V) 28.8±7.1	-	Total As: 100.0±9.5 As(III) 11.1± 2.7 AsB 18.2± 3.4 MMA 13.4± 1.8 DMA 7.1± 2.1 As(V) 50.0± 4.9

(n.d. not detected or below the detection limit)

The extraction efficiencies of each arsenic species in the three consecutive extractions for all extractant tested were similar to those achieved for the first extraction (in both cases the results are expressed as a percentage of each As species with respect to the total As content in the extract). This fact indicates that each As species behaved in a similar way in the different conditions tested. Since total As in the extracts and the sum of each As species quantified were in a good agreement, we concluded that not loss took place on the column.

The As species detected in rice are As(III), followed by DMA and As(V), while MMA is present in a low content.

The Table **3**shows the species detected in the 1:1 methanol: water mixtureextraction for carrot, quinoa and enzymaticextracts for beet by LC-ICP-MS. Extracts were

appropriately diluted in each case. The species for beets, were characterized by spiking the sample with 5 µg L^{-1} of As(III) and As(V).For carrots, only As(III) and As(V) are present. Relative peaks quantification, show about a 50% distribution between the two inorganic As. These results agree with results obtained by previous work[20]. For quinoa, 80% of the As is present as As(V), been the As(V) concentration of As(III) about 20 %. No other species are found in the methanolic fraction. Beets show a different behavior. As species present in this vegetable is only slightly extracted in methanol: water but almost 100% in the enzymatic hydrolysis,were 32% of the As is present as As(V) and mainly an unknown As species about 65% are presented.Sacarose is the sugar extracted from the beets; therefore an As-sacarose or derivatives could be the unknown species.

The Table 3 shows the efficiency of species extraction in soil. The predominant As species in this soil is As(V) (50%) and, in a much lower content (7 – 18%), As(III), DMA and MMA. The sum of theArsenic speciesconcentration (as As) agrees with the total As content in the extract using 1M phosphoric acidas an extractant.

The detection limit for As species within the 3-5 ngg^{-1} range for As(III), 6-8 ngg^{-1} for As(V), 3-5 ngg^{-1} for AsB, 4-5 ngg^{-1} for MMA and 6-7 ngg^{-1} for DMA for the different samples tested. The maximum RSD achieved was about 6%.

No species transformation was detected for the samples tested during the extraction procedure when analyzing the extracts after different extraction times, the same As species were detected although efficiency decreased with time.

Table 4 shows to validate the analytical methodology, the total As content and As species were quantified in the CRM_Sused, Rice Flour NIST 1568a, Tomato Leaves NIST 1573a and Montana II Soil NIST 2711a.

Table 4: The total as content and As species were quantified in the CRM_S extracts

Sample (Total content $mgKg^{-1}$)	Extraction efficiency % Number of extraction	Methanol – Water 1:1	9:1	Enzymatic 1.1-9:1		1M H_3PO_4
Rice Flour	1st	89.0 ± 4.0	80.0 ± 2.0	86.0 ± 3.6	30.3 ± 3.0	-
NIST 1568a	2st	6.0 ± 2.0	7.0 ± 2.6	8.1 ±1.5	5.0 ± 2.5	-
(0.29± 0.03)	**Σ Extractions n=3**					
Tomato Leaves	1st	100.0 ± 4.0	90.0 ± 4.0	98.0 ± 4.6	39.0 ± 4.0	-
	2st	82.0 ± 4.0	52.2 ± 2.8	70.0 ± 4.1	9.9 ± 2.5	-
NIST 1573a	**Σ Extractions n=3**					
	1st	5.1 ± 2.0	7.3 ± 2.4	6.3 ± 2.6	n.d.	-
(0.112 ± 0.004)	2st	90.0 ± 4.7	64.5 ± 2.9	79.2± 5.0	9.9 ± 2.5	-
	Σ Extractions n=3					
Montana II Soil		60.9 ± 5.5	28.9 ± 4.7	50.0 ± 3.9	n.d.	82.9 ± 5.8
NIST 2711a		5.2 ± 1.7	5.4 ± 1.8	4.8 ± 1.3	n.d.	10.0 ±2.0
(107.0 ± 5.0)		66.7 ± 3.3	34.3 ± 4.4	55.8 ± 4.2	n.d.	100.0 ± 8.9

Sample Efficiency (%) As species
Methanolic Extraction (1:1) Enzymatic Extraction1M H_3PO_4

Rice Flour NIST 1568a	Total As: 100.0 ± 4.0 As(III) 28.0 ± 4.3 MMA 3.1 ± 1.6 DMA 62.0 ± 5.0 As(V) 5.9 ± 3.1	Total As: 39.0 ± 4.0 As(III) 12.4± 3.5 MMA 1.8 ± 0.5 DMA 21.4 ± 3.4 As(V) 2.8 ± 1.1	-
Tomato Leaves NIST 1573a	Total As: 90.0 ± 4.7 As(III) 25.1 ± 3.9 MMA 6.3 ± 1.6 DMA 4.2 ± 1.2 As(V) 48.8 ± 7.5	Total As: 9.9 ± 2.5 As(III) 8.2 ±3.3 MMA n.d. DMA n.d. As(V) n.d.	-
Montana II Soil NIST 2711a	Total As: 66.7 ± 3.3 As(III) 11.5 ± 3.0 AsB 12.1 ± 3.6 MMA 10.0 ± 2.7 DMA 8.0 ± 2.9 As(V) 20.7± 4.8		Total As: 100.0 ± 8.9 As(III) 15.9 ± 2.9 AsB 21.5 ± 4.0 MMA 14.0± 3.4 DMA 9.2 ± 3.0 As(V) 38.0 ± 5.5

(n.d. not detected or below the detection limit)

5. Conclusions

All the solutions tested, the different methanol: water mixture extraction were adequate for Arsenic species from rice, carrots and quinoa.

The efficiency related to the nature of the extractant, 1:1 methanol: water being the most adequate mixture for all cases. Three consecutive extractions provided a quantitative recovery of As species. However, for rice an acceptable recovery can be achieved with only one extraction step. As species As(III), As(V), MMA and DMA in 1:1 methanol: water rice extracts remain stable a slight conversion of AsB into DMA was detected However, an important difference between both staples is the fact that the main inorganic species in rice is As(III), while in quinoa it is As(V). Inorganic As(III) and As(V) were the only species present in carrots and quinoa.

The 1M $H_3PO_4$is recommended as an extractant for soil providing an 89% recovery with only one extraction run. The sum of the As species found represents 100% of the As content in all the extracts. As(V) is the most abundant As species found in soil (50%).DMA and MMA are stable in all extractant, while As(III) is gradually oxidized to As(V).

A comparison of the distribution of the As species present in the methanolic extract for carrots and quinoa or in the enzymatic extract for beets (Table 3). No significant transformation of the original As species found in the methanolic or enzymatic solutions.As species present in beets are probably arsenosugars, presumably less toxic, As species toxicity is a factor that should be taken into consideration.

6. Future Scope

More research is still necessary to determine the species present in the beets, where identification is limited by both the availability of standards and the complexity of the matrix.

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