Microchemical Journal 179 (2022) 107541

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Assessment of arsenic in water, rice and honey samples using new and green vortex-assisted liquid phase microextraction procedure based on deep eutectic solvent: Multivariate study

Nail Altunay [a], Adil Elik [a], Muhammad Farooque Lanjwani [b,c], Mustafa Tuzen [b,d,*]

[a] Sivas Cumhuriyet University, Faculty of Science, Department of Chemistry, Sivas, Turkey
[b] Tokat Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department 60250 Tokat, Turkey
[c] Dr M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan
[d] King Fahd University of Petroleum and Minerals, Research Institute, Centre for Environment and Marine Studies, Dhahran 31261 Saudi Arabia

ARTICLE INFO

Keywords:
Vortex-assisted liquid phase microextraction
Deep eutectic solvent
Arsenic
Water
Honey and rice samples
Hydride generation-atomic absorption spectrometry
Factorial design

ABSTRACT

The aim of present study was to determine the arsenic in water, honey and rice samples using a new and green vortex-assisted liquid phase microextraction (VA-LPME), which is based on deep eutectic solvent (DES) by hydride generation-atomic absorption spectrometry. Ethylenediamine-N,N'-disuccinic acid (EDDS) was used as chelating reagent for As(III) ions. Four different DES was prepared by using different combination and molar ratios of hydrogen bond donor (HBD) as benzyltriphenylphosphonium chloride, tetra-n-butylammonium bromide, choline chloride and hydrogen bond acceptor (HBA) groups as ethylene glycol, glycerol and diethanolamine. Different parameters such as pH, chelating agent amount, DES types, molar ratio and its volume, emulsifier agents and its volume, vortex time and sample volume were optimized. The accuracy of the method was confirmed with certified reference materials. The DES-VA-LPME method was validated by using linearity r^2 0.9985, working range 20–600 ng L^{-1}, limit of detection 6.5 ng L^{-1}, limit of quantitation 20 ng L^{-1} and enhancement factor 70. Intra and inter day relative standard deviation was found in the range of 3.6 and 4.1% and 4.2 and 4.9%, respectively. The developed procedure was successfully utilized for determination of arsenic in water, honey and rice samples. The factorial design was used to investigate the individual and combined effects of variables as well significant and insignificant effects.

1. Introduction

Among the many contaminations, arsenic (As) is considered as a very potential of human health and environmental problems in all over the world [1,2]. The Agency for Toxic Substances and Disease Registry (ASTDR), classified arsenic as a first 20 extremely dangerous constituents [3]. The harmfulness of As is closely associated to its oxidation state and speciation. In water, inorganic As types are mostly arsenate (As(V)) and arsenite (As(III)) and organic arsenic are monomethyl arsenic acid (MMA), arsenobetaine and dimethyl arsenic acid (DMA) [4]. Chemical speciation of arsenic generally depends on the pH level and redox potential. Arsenite dominates in the slightly basic water (pH > 7.5) with condensed conditions and As(V) occurs in acidic pH in oxidized conditions [5]. The As (III) is 60 times more poisonous than As(V) and organic arsenic such as DMA and MMA are 70-times less poisonous than inorganic arsenic [6]. The arsenic is very carcinogenic even at low level and many chronic diseases were assessed in people due to the As, such as kidney, lung, skin cancer, liver, papillary, cancer, cortical necrosis, bone weakness, cirrhosis, black-foot disease melanosis [7,8]. Arsenic is an extremely toxic element naturally found in water and aquifer comprise higher level of arsenic due to the As containing salts present in the water. The WHO allowable limits of As in drinking water is 10 μg L^{-1} [9]. Rice is a main component of human diet for about half populations of world. The presence of As in rice is a very serious concern for around 3 billion people all over the world who consumes rice as a main food and millions of peoples may be at risk of As related health issues [10]. The rice is primary source of minerals, vitamins and carbohydrates and it is also most significant food crops in terms of nutrition and calorie intake. Rice is frequently one of the first-choice food for the infants because of its low risk of allergy and palatability [11].

* Corresponding author at: Tokat Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department 60250 Tokat, Turkey.
E-mail address: mustafa.tuzen@gop.edu.tr (M. Tuzen).

https://doi.org/10.1016/j.microc.2022.107541
Received 21 March 2022; Received in revised form 24 April 2022; Accepted 25 April 2022
Available online 28 April 2022

The arsenic come in to agricultural lands through natural sources, like rocks, As-enriched minerals, phosphate fertilisers, anthropogenic sources, coal combustion, herbicides, forest fires, mining, industrial processes and smelting [12]. The average level of arsenic in agricultural that obtain from As-containing pesticides and defoliants ranges between 5 mg kg^{-1} to 2553 mg kg^{-1} [13]. The rice is more affected by higher level of arsenic as compared to other crops and plants. Rice cultivation is carried out in flooded conditions and higher level of arsenic in the land can decrease the production of rice [14]. Honey is natural sweetest food which honeybees composed from nectar of plants and flowers. The honeybees collect this material in their own, store and leave in comb of honey to ripen and mature. Honey is generally monosaccharides fructose and glucose but it also comprises elements, amino acids, pigments waxes, aromatic substances and pollen grains [15]. The arsenic may reach in honey and food chain, animals and humans, either directly by water and air or from soil by accretion in plants used as a food. Arsenic existing in soil may be absorbed through plant roots and translocate to the plant aerial parts comprising pollen [16]. There are many solvents used for remove contamination from samples, out of many solvents' green solvent (deep eutectic solvents (DES), which removes all these contaminations, were synthesized and utilized by scientists. The synthesis of the DES is very fast and easy, generally appropriate two chemicals comprising hydrogen bond acceptors (HBAs, trioctyl ammonium chloride (TOACl), choline chloride (ChCl), tetrabutyl ammonium chloride (TBACl), organic hydroxycarboxcylic acids, hydrogen bond donors (HBDs, sugars, amino acids, polyalcohols) are needed for preparation [17]. Nowadays many extraction methods have been developed to remove the arsenic contaminations. Shishov et al., 2018 reported continuous homogeneous liquid–liquid microextraction (CHLLME) and used for determination of arsenic [18]. Altunay et al., 2019 determined the arsenic by vortex assisted microextraction [19]. Ji et al., 2021 analyzed arsenic in wine samples used ultrasonic-assisted dispersive liquid–liquid microextraction (UA-DLLME) [20]. Ahmed et al., 2021 determination inorganic As in water and food samples by UA-DLLME using CdS nanoflowers [21]. Vicente-Martinez et al., determination of speciation As in water samples by ionic liquid based ispersive liquid–liquid microextraction (IL-DLLME) [22], Zou et al., 2016 determination of speciation As in water samples using Fe3O4@ ZIF-8 nanoparticles [23]. Yinghe et al., 2021 determination of speciation As in wine samples by hydrophobic deep eutectic solvent-based ultrasonic-assisted dispersive liquid–liquid microextraction (HDES-UADLLME) [24].

The main purpose of present study was to determine the arsenic level in water, honey and rice samples using a new and green vortex-assisted liquid phase microextraction procedure based on deep eutectic solvent (DES-VA-LPME) followed by hydride generation-atomic absorption spectrometry. The multivariate study was used to investigate the individual and combined effects of variables as well significant and insignificant effects.

2. Materials and methods

2.1. Chemicals

All chemicals applied in the experiments were of analytical grade and no additional purification steps were applied. Working and calibration standards of As(III) were prepared from a 1000 mg L^{-1} arsenic stock solution which supplied by Guobiao Testing & Certification Co., Ltd (Beijing, China). Ethylenediamine-N,N'-disuccinic acid (EDDS), which used as the chelating agent, purchased from Merck (Darmstadt, Germany) and its desired concentration was prepared through dissolving the proper volume in water. For the preparation of DES, benzyltriphenylphosphonium chloride (Merck), tetra-n-butylammonium bromide (Sigma Aldrich, St. Louis, MO, USA), choline chloride (Sigma), ethylene glycol (Merck), diethanolamine (Merck) and glycerol (Sigma) were used. Ethanol, tetrahydrofuran (THF), acetonitrile and acetone were used as dispersive solvents. For microextraction studies, the pH was optimized in range of 2–9 using borate, phosphate, phthalate, and citrate buffer solutions. 5.0% (w/v) sodium tetra hydroborate ($NaBH_4$) was used as the hydride generation, and this solution was prepared by dissolving of the proper amount in 2.0% (w/v) NaOH. Antifoam 204 (Sigma) in 5.0% (w/v) of HCl was used to prevent foaming in the hydride formation step. All experiments were carried out in ultrapure water, which was achieved from a Milli-Direct Q3 purification scheme (Bedford, MA, USA).

2.2. Instruments

Analysis of arsenic was performed using a hydride generation (HVG-1 3 channels, Shimadzu) atomic absorption spectrometer (HG-AAS) (Shimadzu AAS-6300 model Kyoto, Japan) with a Zeeman effect background correction system. An arsenic hollow cathode lamp was used. Instrumental parameters of the HG-AAS were shown in **Supplementary** Table S1. The digestion of the honey and rice samples was done with microwave system (Milestone Ethos, Italy). Digital pH meter (Metrohm model 654, Herisau, Switzerland), centrifuge (Universal-320, Hettich, London, England) and vortex (VG3 model, IKA GmbH, Germany) were applied to optimize the pH of solutions, to prepare the phase separation and to provide fast and effective dispersion in the microextraction step, respectively.

2.3. Collection of real samples and certified reference materials

Waste water samples were collected in the organized industrial zone in Sivas, Turkey. Well-water was composed from the agricultural region of Sivas. Bottled water samples and rice samples were obtained from local markets in Sivas. Honey samples were collected from the producers in Sivas, Erzincan, Artvin, Erzurum and Rize city, Turkey in between the years 2020–2021. Two certified reference materials CRM (1643e simulated fresh water-trace elements and 1568a rice flour) were used for the validation studies.

2.4. Digestion of samples

2.4.1. Water samples

About 100 mL of the collected water samples were first filtered into the beaker through 0.45 μm membrane filter. Then, water samples were taken on the heating plate and evaporated until approximately 5 mL remained. Finally, the arsenic content was determined by applying the proposed method to the remaining water samples. In addition, directly the suggested process was used to 5 mL of the certified water sample without any pre-treatment.

2.4.2. Rice and honey samples

Rice, honey, and CRM-11568a rice flour samples were prepared by microwave digestion, which previously described in literature [18]. The experimental stages were summarized below. 0.5 g of rice samples, honey and CRM samples were carefully weighed and then shifted to PTFE microwave digestion dishes. Then, 6 mL of 65 % HNO_3 was added to the samples and placed in the microwave system. The microwave system was run at 50% power (600 W) for 12 min and then the samples were cooled for five min. The digestion process continued for 1 min at 50% power (600 W). After the cooling step, the solution was transferred to 25 mL calibrated tubes and the pH was adjusted to 7.0 with NaOH solution. To reduce As(V) to As(III), 2.5 mL of 0.1 mol L^{-1} HCl, 2 mL of 1% KI and 2 mL of 0.2% L-ascorbic acid was added to obtained mixture and then diluted to 25 mL with the water.

2.5. Preparation of DES

The preparation procedure of DESs is green and very simple. It is generally prepared by mixing at least two chemical species containing hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) in a

Table 1
The abbreviation, composition and molar ratio of the DES.

Abbreviation	Composition HBD	HBA	Molar ratio	Refs.
DES-1	benzyltriphenylphosphonium chloride	ethylene glycol	1:1	[25]
DES-2	tetra-n-butylammonium bromide	ethylene glycol	1:1	[26]
DES-3	choline chloride	Glycerol	1:2	[27]
DES-4	choline chloride	diethanolamine	1.4	[28]

Table 2
Analysis of Variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	13	5.20183	0.40014	25.65	0.038
Linear	6	5.06523	0.84421	54.11	0.018
A	1	0.30411	0.30411	19.49	0.048
B	1	1.63246	1.63246	104.63	0.009
C	1	0.15948	0.15948	10.22	0.085
D	1	0.13041	0.13041	8.36	0.102
E	1	1.05627	1.05627	67.70	0.014
F	1	1.78250	1.78250	114.25	0.009
AB	1	0.00055	0.00055	0.04	0.868
AC	1	0.01960	0.01960	1.26	0.379
AD	1	0.01935	0.01935	1.24	0.381
AE	1	0.05157	0.05157	3.31	0.211
AF	1	0.00056	0.00056	0.04	0.868
BD	1	0.04225	0.04225	2.71	0.242
BF	1	0.00272	0.00272	0.17	0.717

definite molar ratio. After adding the reagents, the resulting mixture was placed in water bath and heated to a homogeneous liquid. In this study, four different DES were prepared for efficient, selective and rapid extraction of As(III) from the selected samples. Methods previously reported in the literature were used for the preparation of these DES [25-27]. The abbreviation, composition and preparation conditions of the DES were given in Table 1.

2.6. Proposed DES-VA-LPME procedure

The proposed DES-VA-LPME procedure includes the following experimental steps, respectively. First, 5 mL of the prepared samples in section 2.4 were added to 15 mL conical tubes comprising 10 ng L^{-1} of aqueous As(III) standard solution. A 700 μL of 10^{-4} mol L^{-1} of EDDS was added as chelating reagent and then pH of mixture was optimized to 6.0 with citrate buffer. Next, the resulting solution was sonicated in the ultrasonic bath at room temperature for two min for the complexation of EDDS with As(III). Afterwards, 600 μL of DES-1 with a molar ratio of 1:1 was injected into the EDDS-As complex solution as a result, a cloudy solution was attained. 300 μL of THF was added to the solution as an emulsifier agent and vortexed for 3 min for homogeneous distribution. At this stage, nano/micro-sized emulsion of DES were formed and EDDS-As complexes were then attached to these nano/micro-sized. The DES-rich phase containing EDDS-As complexes was separated from aqueous phase through centrifugation (4000 rpm for 5 min). The aqueous phase was drained using a micropipette. The remaining phase was not suitable for measurement because of its high viscosity and low volume. Therefore, its volume was adjusted up to two mL through acidic ethanol. Finally, absorbance values of As(III) were measured with HG-AAS. All steps were continued in parallel with the sample blank.

2.7. Screening of variables using Plackett-Burman design (PBD)

The experimental Plackett-Burman design (PBD) was utilized to find out the significant effects of experimental factors on the recovery of As (III) [28]. The two-level design was used to screen six factors including vortex time (min), pH of sample solution, chelating agent volume EDDS (μL), DES-1 vol (μL), THF volume (μL), and sample volume (mL) (see Supplementary Table S2). The 16 experimental runs were conducted to investigate the effects of variables on each run (see Supplementary Table S3).

3. Results and discussion

3.1. Factorial design

The subsequent step comprises the optimization of the six significant variables applying response surface approach by PBD method. The PBD is an effective tool usually applied in the investigation of extraction procedures [29]. In present study total of 16 experiments runs were performed (Table 2).

3.1.1. Response surface plots

The statistical experimental design of response surfaces was allowed for the prediction of response function of the variables on the extraction recovery of As(III). The 3D response surface plots were utilized to examine the combined effects of two variables on recovery % of As(III) [27]. The surface plot pH vs chelating agent volume (see Supplementary Figure S1a) indicated highest response was observed at pH 6 and 700 μL chelating agent volume. The surface plot (see Supplementary Figure S1b) indicated good response was obtained at DES-1 vol 600 μL. The Supplementary Figure S1c and Figure S1d described the best response on recovery of As(III) was found at THF volume 300 μL and vortex time 5 min. The surface plot pH vs sample volume (see Supplementary Figure S2a) indicated highest response was observed at lower sample volume 10 mL. The surface plot (see Supplementary Figure S2b) indicated good response was obtained at chelating agent 700 μL and DES-1 vol 600 μL. The Supplementary Figure S2c and Figure S2 d described the best response on recovery of arsenic was obtained at THF volume 300 μL and response was increased at increased the vortex time up to 5 min. The surface plot chelating vs sample volume (see Supplementary Fig. 3a) indicated highest response was observed at lower sample volume 10 mL and 700 μL volume of chelating agent. The surface plot (see Supplementary Figure S3b) indicated highest response was obtained at DES-1 vol 600 μL and THF volume 300 μL. The Supplementary Figure S3c and Figure S3d described the highest surface response on recovery of As(III) was achieved at DES-3 vol 600 μL, vortex time 5 min and 10 mL sample volume. The surface plot showed combined effects of THF volume and vortex time (see Supplementary Figure S4a) and indicated highest surface response was achieved at higher vortex time 5 min and THF volume 300 μL. The surface plot (see Supplementary Figure S4b) showed combined effects THF volume and sample volume and highest surface response was observed at lower samples volume 10 mL. The 3D surface response was used to investigate the combined effects of two variables versus recovery % of As(III) from water, honey and rice water. The highest combined effects were found at higher peak area of response surface plots. As the response increased, the surface area of the plots also increased.

3.1.1.1. Pareto chart. The pareto plot was derived from the multivariate examination. The bar height of pareto plot is directly related to absolute value of predictable standardized effects and the vertical line indicates significant effects at the 95% confidence level [28]. The four variables including (A) pH, (B) chelating agent volume, (E) vortex time and (F)

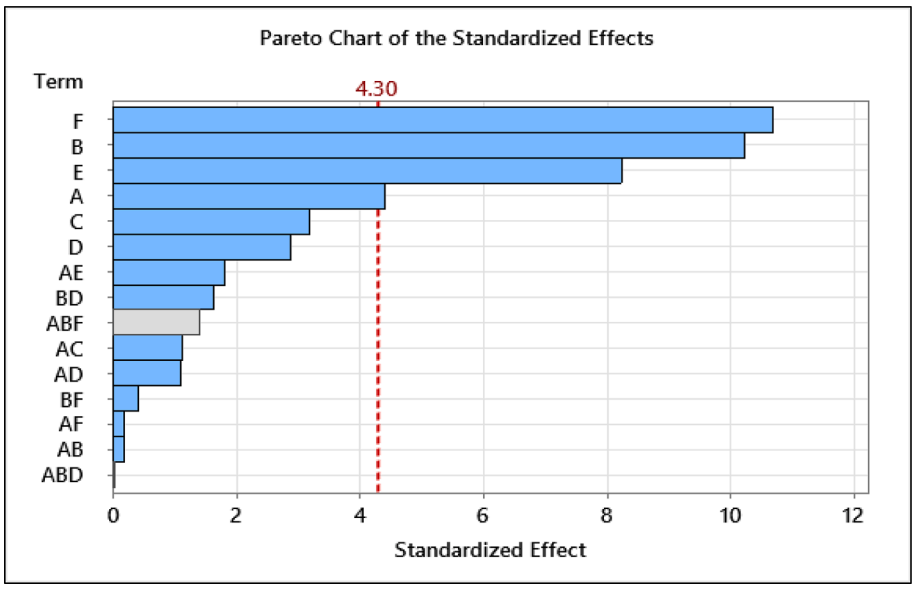

Fig. 1. Pareto chart of variables.

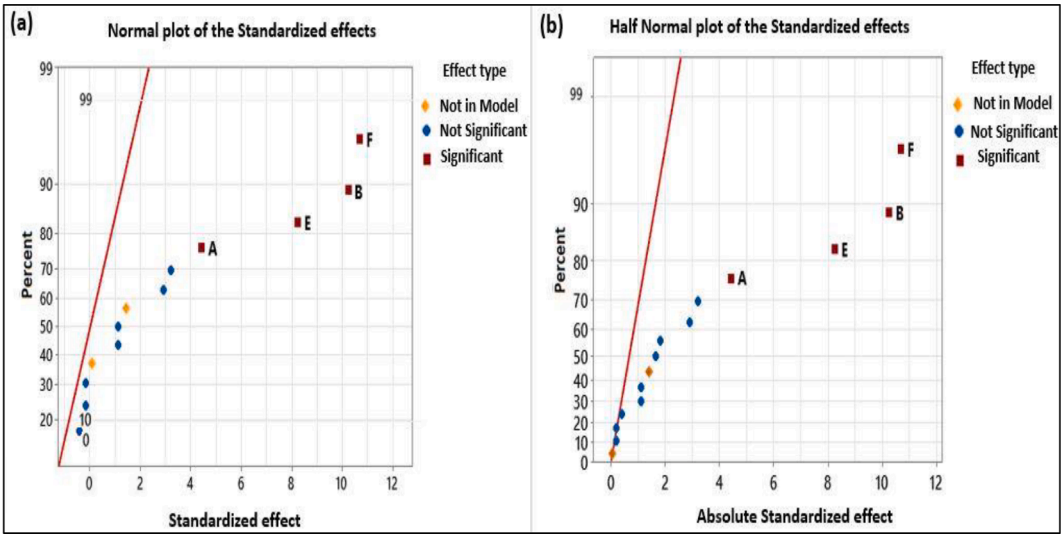

Fig. 2. (a) Normal probability and (b) half normal probability plot.

sample volume was crossed the vertical line and considered as a significant effect on recovery of As(III) from water, rice honey samples (see Fig. 1). The other variables did not cross the vertical line and showed no significant effects on the recovery of As(III) from water, honey and rice samples.

3.1.1.2. Analysis of variance ANOVA. The ANOVA analysis was carried on the basis of P-value at 95% confident interval. The experimental model is significant when p-value of model is less than (<0.05) at 95% confidence level and if P-value is higher than (>0.05) the variable is no significant [30]. The ANOVA (see Table 25) was based of F-value and P-value. The F-values were varied from 0.04 to 114.25 and P-value was found in ranged 0.009 to 0.868. The P-value of variable (A) pH, (B) chelating agent volume, (E) vortex time and (F) sample volume was less than (<0.05) and observed as significant effects on the recovery of As (III) in water, rice and honey samples. The other variables indicated P-value higher than (>0.05) and observed as a no significant effects on the recovery of As(III). It was observed that F-value and P-values were inversely proportional to each other because when F-value increased P-value was decreased and when F-value was lower P-values were observed higher.

3.1.1.3. Normal and half normal plots. The normal probability and half normal plots of standardized residual were applied to investigate the significant and no significant effects of factors on the recovery of As(III) from water, rice and honey samples [31] The normal probability and half normal plots (see Fig. 2a and 2b) indicated that four variables including A, B, E and F shows significant effects and good fit on the recovery of As(III) and other factors were showed no significant effects on the recovery of As(III).

3.1.1.4. Residual plots. The residual plots of standardized residual and observed value (see Fig. 3a and 3b) indicated all points randomly falls away from the horizontal reference line and showed significant effects on the recovery of As(III) from water, honey and rice samples. The histogram (see Fig. 3c) clearly described the vertical bar lines randomly falls in both negative as well as positive sides which showed significant and no significant effects on the recovery of As(III). The residual plots

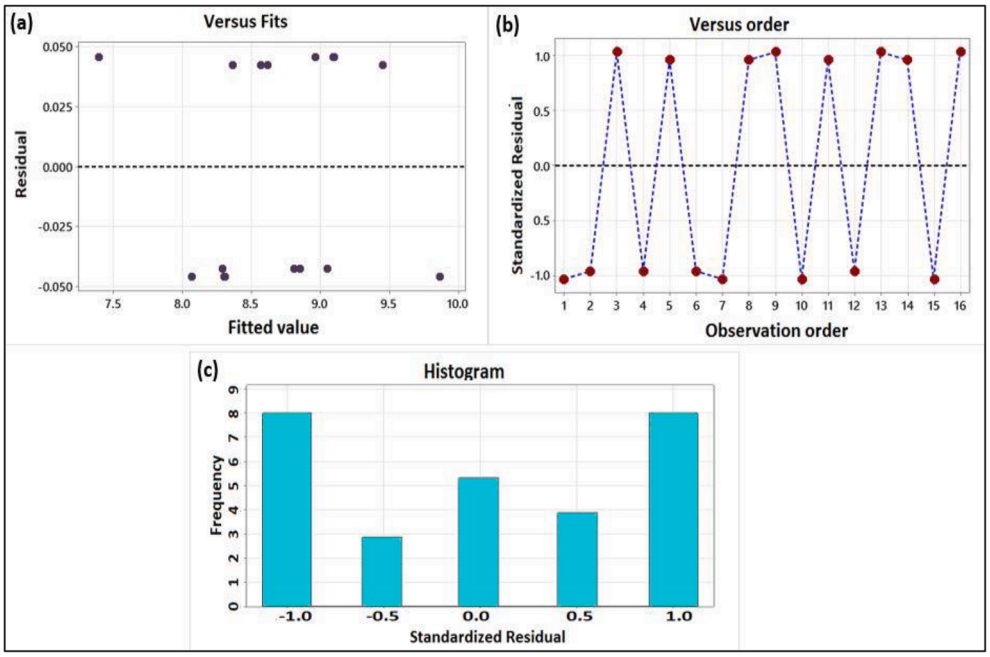

Fig. 3. Residual plots (a-c).

revealed that the model was good fitted on the recovery of As(III).

3.2. Effects of parameters on the recovery of As(III)

The pH level of solution plays a vital role in microextraction investigation. The interaction between As(III)/(V) and the chelating reagent may vary depending on the pH level of the solution. In addition, pH level may effect on both formation DES solvent and microextraction of the sample solution. Hence, the effect of pH value on extraction of As(III)/(V) was examined in range 2 to 9 and pH was adjusted by buffer solutions (see Supplementary Figure S5). The results indicated that pH did not observed particular effects on the recovery of As(V) but recovery of As(III) depend on the pH level of the solution and better recovery of As (III) was observed at pH 6. Therefore, pH 6 was selected as an optimum for further study for extraction recovery of As(III) in water, rice and honey samples.

The chelating agent help to increase the extraction recovery of As(III) in samples solution. Present study 150 to 1000 μL EDDS volume was used for recovery of As(III) and results showed the recovery of arsenic was increase when increase the volume of EDDS up to 700 μL (see Supplementary Figure S6). The results revealed that higher volume of chelating agent could improve the recovery of arsenic from water, honey and rice samples. Therefore, EDDS volume 700 μL was selected for further research work.

Table 3
Quantitative characteristics of the DES-VA-LPME procedure for the analysis of As(III) ions in selected sample.

Parameters	Optimum values
Working range (ng L^{-1})	20–600
R^2	0.9985
[a]LOD (ng L^{-1})	6.5
[b]LOQ (ng L^{-1})	20
EF	70
PF	75
[c]Intra-day (RSD %)	3.6 and 4.1
[c] Inter-day (RSD %)	4.2 and 4.9

[a] detection limits were estimated based on 3Sb/m.
[b] limit of quantification were estimated based on 10Sb/m.
[c] Relative standard deviation (C = 50 and 100 ng L^{-1} of As(III) ion, n = 5).

The amount and composition of the DES solvent were main factors in attaining effective recovery of arsenic in different samples. The DES solvents were frequently used in the microextraction because of it has interesting properties like low density, commercially available, green and higher dissolubility. Hence, four different types of DES solvents such as DES-1, DES-2, DES-3 and DES-4 were utilized in recovery of As(III) (see Supplementary Figure S7). The results indicated that DES-1 solvent showed good recovery of As(III) as compared to other DES solvents. The five different DES solvent molar ratios of optimized DES-1 were utilized and molar ratio of benzyltriphenylphosphonium chloride and ethylene glycol was 3:1, 2:1, 1:1, 1:2, 1:2 and result indicated the at molar ratio 1:1 showed better recovery of arsenic as compared to other molar ratios (see Supplementary Figure S8). The DES solvent molar ratio 1:1 was optimized for further study. The different volume of DES-1 solvent 150 to 900 μL were used to investigate the recovery of As(III) and results indicated the DES-1 vol 600 μL observed better recovery of As(III) from samples (see Supplementary Figure S9). Therefore, DES-1 vol 600 μL was optimized for further study.

Emulsifier agents are a surface-active ingredient that absorb at freshly designed oil–water interface through emulsion preparation and it protects the freshly shaped droplets against intermediate recoalescence. The four different types of emulsifier agents like ethanol, THF, acetonitrile and acetone were applied in present study to examine the recovery of As(III) from samples (see Supplementary Figure S10). The results revealed that emulsifier agent THF showed better recovery of As (III) and was optimized for further study·THF volume was optimized in the range of 100–500 μL for the recovery of As(III) (see Supplementary Figure S11). The result indicated the maximum recovery of arsenic was found at THF volume 300 μL and was optimized for further experimental work.

Different vortex time was applied investigate the recovery of As(III) and vortex time was varied from 0 to 5 min (see Supplementary Figure S12). The observed result indicated that maximum recovery of As (III) was found at vortex time 5 min and results revealed the recovery of As(III) was increased with increases the vortex time.

The different volume of sample 10 to 250 mL was used for recovery of As(III) and results indicated that recovery of As(III) inversely proportional to the volume of sample (see Supplementary Figure S13).

Table 4
Tolerance limit of interferent/As(III) ratio in determination of 200 ng L^{-1} of As (III) using the DES-VA-LPME procedure (N = 3).

Species	*Tolerable limit	Recovery (Mean ± standard deviations)
Ca^{2+}	1000	99 ± 3
Mg^{2+}	1000	99 ± 4
K^{+}	1000	99 ± 4
Na^{+}	1000	98 ± 2
$C_2O_4^{2-}$	1000	98 ± 2
PO_4^{3-}	750	98 ± 3
As^{5+}	750	97 ± 3
SO_4^{2-}	750	98 ± 2
Hg^{2+}	750	97 ± 3
Pb^{4+}	700	96 ± 5
Cr^{3+}	500	96 ± 3
Fe^{3+}	500	97 ± 2
Pb^{2+}	500	96 ± 3
Zn^{2+}	500	96 ± 4
Mn^{2+}	250	95 ± 2
Co^{2+}	250	96 ± 3
Ni^{2+}	250	97 ± 2
Cu^{2+}	250	96 ± 3
Al^{3+}	250	96 ± 4
Cd^{2+}	250	97 ± 4
Se^{6+}	250	96 ± 5
Sb^{3+}	100	95 ± 5

*[Ions amount]/ [As(III) amount].

When increase the volume of sample recovery % was decreased, its mean recovery of As(III) directly depends on the volume of sample used for extraction recovery.

3.3. Method validation

The reliability of analytical method is depended on the various terms of linearity, working range, limit of detection (LOD), enhancement factor (EF), limit of quantitation (LOQ), preconcentration factor (PF), inter-day and intra-day study and relative standard deviation (RDS%) (see Table 3). The LOD and LOQ, which are determined as 3 s/m and 10 s/m, respectively (s and m were standard deviation of the reagent blank, and slope of a calibration graph, respectively). The EF was calculated from the ratio of the slopes of the calibration graphs obtained before and after the present method. The PF was calculated as ratio of maximum sample volume to minimum final volume. The proposed DES-VA-LPME method showed good linearity r^2 value 0.998 and working range was 20–600 ng L^{-1}. The LOD and LOQ values were 6.5 and 20 ng L^{-1}, respectively. PF and EF values were found 75 and 70. The inter-day and intra-day value was found 3.6 to 4.2%, respectively.

3.4. Effects of matrix ions

Tolerance limit of foreign ions is defined as ion concentration causing a negative effect lower than 5 % under optimum conditions. The foreign ions play a vital role for the extraction and determination of arsenic ions in DES-VA-LPME method. Tolerance limit of matrix components were found 100 and 1000-fold higher than analyte ions (200 ng L^{-1}) (see Table 4). The obtained results showed that no particular effects were observed of foreign ions. Therefore, developed method is highly effective for extraction and determination of arsenic from water, honey and rice samples.

3.5. Determination of total arsenic in certified reference materials, rice and honey samples

The accuracy of the DES-VA-LPME method was confirmed with analyzing of certified reference materials. The certified and experimental values were found 0.285 ± 0.014 mg kg^{-1} and 0.281 ± 0.008 mg kg^{-1} in CRM-1568a rice flour. Recovery values were found 98.5 %.

Table 5
Determination of total arsenic in certified reference materials (N = 5).

Reference materials	Validation parameters	Experimental data
CRM-1568a rice flour	Certified value (mg kg^{-1})	0.285 ± 0.014
	Found value (mg kg^{-1})	0.281 ± 0.008
	Recovery (%)	98.5
	*$t_{exp.}$	1.11
CRM-1643e simulated fresh water-trace elements	Certified value (μg L^{-1})	60.45 ± 0.72
	Found value (μg L^{-1})	59.31 ± 2.24
	Recovery (%)	98.1
	*$t_{exp.}$	1.19

Table 6
The amount of total arsenic in rice and honey samples (N = 3).

Sample	Found value (μg g^{-1})
Brown rice-1	0.374 ± 0.05
Brown rice-2	0.319 ± 0.04
White rice-1	0.139 ± 0.02
White rice-2	0.127 ± 0.02
Honey from Sivas city	n.d*
Honey from Erzurum city	0.095 ± 0.01
Honey from Artvin city	n.d
Honey from Erzincan city	0.142 ± 0.01
Honey from Rize city	nd

*could not be determined.

Table 7
Recovery obtained from the determination of As(III) in water samples (N = 3).

Samples	Added (ng L^{-1})	Found (ng L^{-1})	RSD (%)	Recovery (%)
Waste water-1	–	45.1	3.4	–
	100	140.8	4.1	95.7
Waste water-2	–	75.9	2.7	–
	100	172.0	3.9	96.1
Waste water-3	–	62.7	2.6	–
	100	160.2	3.3	97.5
Well-water-1	–	22.8	2.1	–
	100	121.2	3.5	98.4
Well-water-2	–	n.d*	–	–
	100	96.3	3.7	96.3
Bottled water-1	–	n.d*	–	–
	100	95.0	2.6	95.0
Bottled water-2	–	n.d*	–	–
	100	96.6	3.4	96.6

*could not be determined.

The certified and experimental values were found 60.45 ± 0.72 μg L^{-1} and 59.31 ± 2.24 μg L^{-1} in CRM-1643e simulated fresh water-trace elements with 98.1 % recovery (see Table 5).

The different rice and honey samples were taken and applied to present method for the determination of total arsenic (see Table 6). Arsenic concentration in analyzed rice samples were found in the range of 0.127 to 0.374 μg g^{-1}. The results of arsenic in honey samples were found between 0.095 and 0.142 μg g^{-1}.

3.6. Application to water samples

The DES-VA-LPME method was successfully applied to waste water, well water, and bottled water samples for the determination of As(III) ions. Standard addition method was applied to water samples and quantitative recovery values were found. RSD and recovery values were found in the range of 2.1–4.1 % and 95–98.4 %, respectively (see Table 7).

Table 8
Comparison the present method with reported methods.

Instruments	Method	LOD	LOQ	LR	ER (time min)	PF, EF	RSD%	References
HG-AAS	DES-VAME	7.5 ng L^{-1}	16.6 ng L^{-1}	15–350 ng L^{-1}	3.0	104	2.1	[19]
FAAS	UA-DLLME	0.3 ng L^{-1}	1.0 ng L^{-1}	2.0–50 ng L^{-1}	2–10	61	2.7–5.5	[20]
AAS	In situ IL-DLLME	0.01 ng mL^{-1}	0.0.034 ng mL^{-1}	0.2–15 ng mL^{-1}	20	200	3.2	[32]
ICP-MDS	SPE	14.3 μg L^{-1}	47.3 μg L^{-1}	1.0–1.8 μg L^{-1}	10	158	7.5	[33]
ICP-MS	Chip-based- MSPME	4.8 ng L^{-1}	8.6 ng L^{-1}	0.02–20 ng L^{-1}	10	23	5.2	[34]
ETAAS	DLLME	0.02 μg L^{-1}	0.05 μg L^{-1}	0.05–0.8 μg L^{-1}	0–15	295	4.8	[22]
ETAAS	LLME	17 ng L^{-1}	56 ng L^{-1}	0.05–13 μg L^{-1}	0–10	35	3.1	[35]
ETAAS	DESUALPME	10 ng L^{-1}	33 ng L^{-1}	200–500 μL	1–15	25	4.3	[36]
HR CS ETAAS	MSPE	0.25 ng L^{-1}	0.82 ng L^{-1}	2.3 mL min^{-1}	2.0	23.4	2.2	[37]
ICP OES	DES	0.009–0.1 μg g^{-1}	0.03–0.3 μg g^{-1}	0.9–1.3 μg g^{-1}	5–45	100	0.9–3.7	[38]
HG-AAS	VA-LPME	6.5 ng L^{-1}	20 ng L^{-1}	20–600 ng L^{-1}	0–5	75,70	2.2–4.1	**Present work**

Deep eutectic solvent extraction by vortex-assisted liquid phase microextraction (DES-VA-LPME), Inductively coupled plasma optical emission spectrometer (ICP OES), Hydride generation atomic absorption spectrometry (HG-AAS), Flame Atomic absorption spectrophotometer (FAAS), In situ ionic liquid dispersive liquid liquid microextraction (In situ IL-DLLME), Magnetic solid phase extraction (MSPE), Chip-based magnetic solid phase microextraction (MSPME), Solid phase extraction (SPE), Deep eutectic solvent (DES), Deep eutectic solvent ultrasound-assisted liquid phase microextraction (DESUALPME), Hydride generation with high resolution continuum source electrothermal atomic absorption spectrometry (HR CS ETAAS), Electrothermal atomic absorption spectrometry (ETAAS), Ultrasonic-assisted dispersive liquid–liquid microextraction (UA-DLLME), Deep eutectic solvent (DES) based vortex assisted microextraction (DES-VAME), Limit of detection (LOD), Limit of quantification (LOQ), Linear range (LR), Extraction recovery time (ER), Pre-concentration factor (PF), Enrichment factor (EF), Relative standard deviation (RSD).

4. Conclusions

The simple, rapid and green vortex-assisted liquid phase microextraction procedure based on deep eutectic solvent (DES-VA-LPME) was applied to water, rice and honey samples by using hydride generation-atomic absorption spectrometry (HGAAS). Developed analytical method was selective and sensitive for the extraction and determination of arsenic ions. The factorial design was successfully applied to access the individual as well as combined effects of variables of the recovery of arsenic ions. The present developed method was compared with other developed methods all over the world (see Table 8). The present DES-VA-LPME has some advantages such as low RSD, LOD, LOQ, short extraction time, high PF and EF and long linear range according to literature values. Tolerance limits of foreign ions were found high. Present method can be applied to routine studies for the determination of arsenic ions in water, rice, honey and complex environmental and food samples.

CRediT authorship contribution statement

Nail Altunay: Investigation, Validation, Writing – original draft, Writing – review & editing, Software. **Adil Elik:** Writing – original draft, Writing – review & editing, Software. **Muhammad Farooque Lanjwani:** Investigation, Writing – original draft, Writing – review & editing, Software. **Mustafa Tuzen:** Investigation, Validation, Writing – original draft, Writing – review & editing, Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Muhammad Farooque Lanjwani would like to thanks to Turkey Bursary for financial supports. Dr. M. Tuzen also thanks to Turkish Academy of Sciences (TUBA) for partial supports.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2022.107541.

References

[1] F.R. Amin, Y. Huang, Y. He, R. Zhang, G. Liu, C. Chen, Biochar applications and modern techniques for characterization, Clean Techn Environ Policy 18 (5) (2016) 1457–1473.
[2] M. Raza, F. Hussain, J.Y. Lee, M.B. Shakoor, K.D. Kwon, Groundwater status in Pakistan: A review of contamination, health risks, and potential needs, Critical Reviews in Environmental Science and Technology. 47 (18) (2017) 1713–1762.
[3] R. Amen, H. Bashir, I. Bibi, S.M. Shaheen, N.K. Niazi, M. Shahid, J. Rinklebe, A critical review on arsenic removal from water using biochar-based sorbents: the significance of modification and redox reactions, Chemical Engineering Journal. 396 (2020), 125195.
[4] J.I. LeMonte, J.W. Stuckey, J.Z. Sanchez, R. Tappero, J. Rinklebe, D.L. Sparks, Sea level rise induced arsenic release from historically contaminated coastal soils, Environmental Science & Technology. 51 (11) (2017) 5913–5922.
[5] K.K. Jinadasa, E. Peña-Vázquez, P. Bermejo-Barrera, A. Moreda-Piñeiro, New adsorbents based on imprinted polymers and composite nanomaterials for arsenic and mercury screening/speciation: A review, Microchemical Journal 156 (2020), 104886.
[6] M.B. Shakoor, N.K. Niazi, I. Bibi, G. Murtaza, A. Kunhikrishnan, B. Seshadri, M. Shahid, S. Ali, N.S. Bolan, Y.S. Ok, M. Abid, F. Ali, Remediation of arsenic-contaminated water using agricultural wastes as biosorbents, Critical Reviews in Environmental Science and Technology. 46 (5) (2016) 467–499.
[7] L. Joseph, B.M. Jun, J.R. Flora, C.M. Park, Y. Yoon, Removal of heavy metals from water sources in the developing world using low-cost materials: A review, Chemosphere. 229 (2019) 142–159.
[8] V. Antoniadis, S.M. Shaheen, E. Levizou, M. Shahid, N.K. Niazi, M. Vithanage, J. Rinklebe, A critical prospective analysis of the potential toxicity of trace element regulation limits in soils worldwide: Are they protective concerning health risk assessment?-A review, Environment international. 127 (2019) 819–847.
[9] M.F. Lanjwani, M.Y. Khuhawar, T.M. Jahangir Khuhawar, A.H. Lanjwani, M. S. Jagirani, A.H. Kori, J., Muhammad Dodo, Risk assessment of heavy metals and salts for human and irrigation consumption of groundwater in Qambar city: a case study, Geology, Ecology, and Landscapes. 4 (1) (2020) 23–39.
[10] J.K. Biswas, M. Warke, R. Datta, D. Sarkar, Is arsenic in rice a major human health concern, Current Pollution Reports. 6 (2) (2020) 37–42.
[11] C.J. Henry, What children eat in developing countries: diet in the etiology of undernutrition, In Nurturing a Healthy Generation of Children: Research Gaps and Opportunities. 91 (2019) 43–53.
[12] M.S. Rahaman, M. Akter, M.M. Rahman, M.T. Sikder, T. Hosokawa, T. Saito, M. Kurasaki, Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism, Environmental Toxicology and Pharmacology. 74 (2020), 103302.
[13] T. Abedi, A. Mojiri, A., Arsenic uptake and accumulation mechanisms in rice species, Plants. 9 (2) (2020) 129.
[14] S. Awasthi, R. Chauhan, S. Srivastava, R.D. Tripathi, The journey of arsenic from soil to grain in rice, Frontiers in Plant Science. 8 (2017) 1007.
[15] M.F. Lanjwani, F.A. Channa, Minerals content in different types of local and branded honey in Sindh, Pakistan, Heliyon. 5 (7) (2019) e02042.
[16] N.M. Zarić, S. Braeuer, W. Goessler, Arsenic speciation analysis in honey bees for environmental monitoring, Journal of Hazardous Materials. 432 (2022) 128614.
[17] A.H. Panhwar, M. Tuzen, T.G. Kazi, Deep eutectic solvent based advance microextraction method for determination of aluminum in water and food samples: Multivariate study, Talanta. 178 (2018) 588–593.
[18] A. Shishov, M. Wieczorek, P. Kościelniak, D. Dudek-Adamska, A. Telk, L. Moskvin, A. Bulatov, An automated continuous homogeneous microextraction for the determination of selenium and arsenic by hydride generation atomic fluorescence spectrometry, Talanta. 181 (2018) 359–365.

[19] N. Altunay, A. Elik, R. Gürkan, Innovative and practical deep eutectic solvent based vortex assisted microextraction procedure for separation and preconcentration of low levels of arsenic and antimony from sample matrix prior to analysis by hydride generation-atomic absorption spectrometry, Food Chemistry. 293 (2019) 378–386.
[20] Y. Ji, M. Zhao, A. Li, L. Zhao, Hydrophobic deep eutectic solvent-based ultrasonic-assisted dispersive liquid-liquid microextraction for preconcentration and determination of trace cadmium and arsenic in wine samples, Microchemical Journal. 164 (2021), 105974.
[21] H. Ahmad, L. Zhao, C. Liu, C. Cai, F. Ma, Ultrasound assisted dispersive solid phase microextraction of inorganic arsenic from food and water samples using CdS nanoflowers combined with ICP-OES determination, Food Chemistry. 338 (2021), 128028.
[22] Y. Vicente-Martinez, M. Caravaca, A. Soto-Meca, Non-chromatographic speciation of arsenic by successive dispersive liquid-liquid microextraction and in situ formation of an ionic liquid in water samples, Microchemical Journal. 157 (2020), 105102.
[23] Z. Zou, S. Wang, J. Jia, F. Xu, Z. Long, X. Hou, Ultrasensitive determination of inorganic arsenic by hydride generation-atomic fluorescence spectrometry using Fe3O4@ ZIF-8 nanoparticles for preconcentration, Microchemical Journal. 124 (2016) 578–583.
[24] Y. Ji, M. Zhao, A. Li, L. Zhao, Hydrophobic deep eutectic solvent-based ultrasonic-assisted dispersive liquid-liquid microextraction for preconcentration and determination of trace cadmium and arsenic in wine samples, Microchemical Journal. 164 (2021) 105974.
[25] R.K. Ibrahim, M. Hayyan, M.A. AlSaadi, S. Ibrahim, A. Hayyan, M.A. Hashim, Physical properties of ethylene glycol-based deep eutectic solvents, Journal of Molecular Liquids. 276 (2019) 794–800.
[26] A.P. Abbott, R.C. Harris, K.S. Ryder, Application of hole theory to define ionic liquids by their transport properties, The Journal of Physical Chemistry B. 111 (18) (2007) 4910–4913.
[27] F.S. Mjalli, G. Murshid, S. Al-Zakwani, A. Hayyan, Monoethanolamine-based deep eutectic solvents, their synthesis and characterization, Fluid Phase Equilibria. 448 (2017) 30–40.
[28] E. Tsanaktsidou, C.K. Markopoulou, P.D. Tzanavaras, C.K. Zacharis, Homogeneous liquid phase microextraction using hydrophilic media for the determination of fluoroquinolones in human urine using HPLC-FLD, Microchemical Journal. 172 (2022), 106906.
[29] N. Altunay, Optimization of ultrasound-assisted dispersive liquid–liquid microextraction of niacinamide in pharmaceutical and cosmetic samples using experimental design, Microchemical Journal. 170 (2021), 106659.
[30] H. Taşpınar, A. Elik, S. Kaya, N. Altunay, Optimization of green and rapid analytical procedure for the extraction of patulin in fruit juice and dried fruit samples by air-assisted natural deep eutectic solvent-based solidified homogeneous liquid phase microextraction using experimental design and computational chemistry approach, Food Chemistry. 358 (2021), 129817.
[31] Y. Ding, M. Sartaj, Statistical analysis and optimization of ammonia removal from aqueous solution by zeolite using factorial design and response surface methodology, Journal of Environmental Chemical Engineering. 3 (2) (2015) 807–814.
[32] V. Ashouri, K. Adib, G.A. Fariman, M.R. Ganjali, M. Rahimi-Nasrabadi, Determination of arsenic species using functionalized ionic liquid by in situ dispersive liquid-liquid microextraction followed by atomic absorption spectrometry, Food Chemistry. 349 (2021), 129115.
[33] E. Yilmaz, Z. Erbas, M. Soylak, Hydrolytic enzyme modified magnetic nanoparticles: An innovative and green microextraction system for inorganic species in food samples, Analytica Chimica Acta. 1178 (2021), 338808.
[34] Z. Chen, B. Chen, M. He, B. Hu, Magnetic metal-organic framework composites for dual-column solid-phase microextraction combined with ICP-MS for speciation of trace levels of arsenic, Microchimica Acta. 187 (1) (2020) 1–9.
[35] M.N. Oviedo, E.F. Fiorentini, A.A. Lemos, M.B. Botella, R.G. Wuilloud, Two-step separation and determination of inorganic as species in water, soil and sediment samples by implementing two ionic liquids in dispersive liquid–liquid microextraction with electrothermal atomic absorption spectrometry detection, Microchemical Journal. 159 (2020) 105386.
[36] R.A. Zounr, M. Tuzen, M.Y. Khuhawar, Ultrasound assisted deep eutectic solvent based on dispersive liquid liquid microextraction of arsenic speciation in water and environmental samples by electrothermal atomic absorption spectrometry, Journal of Molecular Liquids. 242 (2017) 441–446.
[37] A.C. Valdivia, M.L. Guerrero, E.V. Alonso, J.C. Pavón, A.G. de Torres, Determination of As, Sb and Hg in water samples by flow injection coupled HR CS ETAAS with an in situ hydride generator, Microchemical Journal. 138 (2018) 109–115.
[38] J.M. Matong, L. Nyaba, P.N. Nomngongo, Determination of As, Cr, Mo, Sb, Se and V in agricultural soil samples by inductively coupled plasma optical emission spectrometry after simple and rapid solvent extraction using choline chloride-oxalic acid deep eutectic solvent, Ecotoxicology and Environmental Safety. 135 (2017) 152–157.

Further reading

[39] O. Viegas, C. Esteves, J. Rocha, A. Melo, I.M. Ferreira, Simultaneous determination of melatonin and trans-resveratrol in wine by dispersive liquid–liquid microextraction followed by HPLC-FLD, Food Chemistry. 339 (2021), 128091.