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Therefore, speciation and determination of arsenic in human blood and water samples is very important [3]. The toxicity of arsenic compounds is generally linked to the soluble inorganic trivalent forms, which is controlled by pH. Human exposure assessment in workers to arsenic containing substances includes short term (recent or acute exposure) and long term (chronic exposure) tests that can be performed to monitor detoxification efficiencies. Exposure of arsenic can lead to progressive peripheral and central nervous changes, such as, numbness and muscle tenderness. Normal arsenic concentrations in blood and urine are typically below 50 µg L\(^{-1}\) and 7 µg L\(^{-1}\), respectively [4]. Threshold limit value

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A novel analytical method based on centrifuging dispersive liquid-liquid microextraction (CD-LLME) procedure for pre-concentration of As (III) has been developed prior to determine by hydride generation atomic absorption spectrometry (HG-AAS). In this method, 0.1 g of a task specific ionic liquids (methyltrioctylammonium 2-mercaptobenzoate; TOMAS; TSIL) as the extracting and complexing solvent and acetone as dispersant solvent were rapidly added into the water and blood samples at pH 4.5. The As (V) is simply calculated by difference between total concentration and inorganic forms As (III) in liquid samples. By optimizing parameters, the enrichment factor (EF) was obtained 9.8 and 49.6 for blood and water samples, respectively. The limit of detection (LOD) of 22.4 ngL\(^{-1}\) and 4.3 ngL\(^{-1}\) were achieved for 10 mL and 50 mL of As(III) in blood and water samples, respectively (RSD<\%5). The real samples were validated by certified reference material (CRM) by proposed procedure.

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**ARTICLE INFO:**
Received 22 Aug 2019
Revised form 3 Nov 2019
Accepted 28 Nov 2019
Available online 27 Dec 2019

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**Keywords:**
Arsenic speciation,
Water and human blood,
Task-specific ionic liquids,
Centrifuging dispersive liquid-liquid microextraction

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**1. Introduction**
Analytical methods has important role for determining hazardous heavy metal in different matrices such as human blood and environmental samples. Analytical methods based on nanotechnology and ionic liquids was used for determination arsenic concentration in the blood, urine and serum samples by different instruments such as ICP-MS, ET-AAS and HG-AAS [1]. Inorganic arsenic compounds are toxic in human body but organic arsenic is usually less harmful [2].
(TLV) of arsenic concentration in human blood is less than 2.5 μg dL⁻¹ [5].

So, the sensitive analytical techniques, such as; high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS)[6], inductively coupled plasma atomic emission spectrometry (ICP-AES)[7], Cold vapor/hydride generation atomic absorption spectrometry (HG-AAS)[8], hydride generation and atomic fluorescence spectrometry (HGAFS)[9] and electro-thermal atomic absorption spectrometry (ET-AAS)[10]. Gas Chromatography-Inductively Coupled Plasma-Mass Spectrometry (GC-ICP-MS) or Ion Chromatography Coupled to inductively coupled plasma mass spectrometry (IC-ICP-MS) was required for determination and speciation of arsenic in blood and water samples. Among them, HG-AAS is a conversional instrument which was widely used for arsenic determination in human biological samples and waters. But, sample preparation was needed for preconcentration and separation ions from real samples before using analytical techniques. The ionic liquids (ILs) as green solvent were used for separation and determination metals in liquid phases. The different hydrophobic/hydrophilic ILs can be extracted ions from waters with ligand by spectrometry methods [11-14]. The cadmium, chromium and mercury were removed from water samples by TSILs. The sample preparation procedures based on ionic liquids (ILs) was used for this purposed. Recently, the liquid–liquid extraction (LLE)[15], cloud point extraction (IL-CPE)[16], ionic liquid based on solid phase extraction (IL-SPE) [17] was reported by previous papers. Arsenic speciation and determination by GC-ICP-MS or IC-ICP-MS were too much expensive. On the other hands, the arsenic speciation with conversional instruments needs to prepare difficult samples at low time. In this study, a new analytical method based on TOMAS (C₃₂H₅₉NO₂S) was used for arsenic speciation in water and human blood samples by CD-LLME procedure. Based on results, many advantages such as, low time, efficient extraction and high recovery were obtained.

2. Experimental
2.1. Apparatus
The experiments were performed using a GBC-932 atomic absorption spectrometer equipped with a cold vapor/hydride generation module (HG3000-AAS-AUS). The operating parameters for the metal of interest were set as recommended by the manufacturer. Mercury and arsenic determined by HGAAS respectively. Arsenic hollow cathode lamp based on 8 mA, 193.7 nm and the spectral bandwidth of 1 nm was used. The pH values of the solutions were measured by a digital pH meter (Metrohm 744). In all analysis the deuterium background correction was turn on (Table 1). The instrumental calibration curve was linear between 0.5 –30 μg L⁻¹. All containers (quartz crucibles, plastic tubes) were cleaned with detergent and treated successively by the HNO₃ (2%) and rinsed with de-ionized water (DW). The pure argon gas (99.99%) was used as a carrier gas for HGAAS analysis. The reduced flame was turn on by HG-AAS.

2.2. Materials
All chemicals of analytical grade such as nitric acid, hydrochloric acid, Polyoxyethylene octyl phenyl ether (TX-100), sodium acetate, sodium hydroxide, and sodium borohydride (NaBH₄) were from Merck Germany. Reducing agents (aqueous solution of 0.6% sodium borohydride in 0.5% sodium hydroxide) were prepared freshly and filtered before use. Arsenic standard solutions were prepared from a stock solution of 1000 mg L⁻¹ as ultra-trace in 2% nitric acid from Fluka Switzerland (No; 39436). Working standard solutions were prepared by dilution of stock and intermediate standards. Buffer solutions were prepared from 1-2 mol L⁻¹ sodium acetate and acetic acid for pH=3-7. Ultrapure water was obtained from a Water System of Iranian research Institute of Petroleum Industry (Millipore RIPI), Alderich. The TSIL, Ethyltrioctylammonium 2-mercaptobenzoate or Trioctylmethylammonium thiosalicylate (TOMAS, CAS Number 1027004-61-0) was purchased from Sigma Aldrich.
Table 1. Instrumental Conditions for arsenic

| Parameter | Arsenic |
|-----------|---------|
| Wavelength (nm) | 193.7 |
| Lamp current (mA) | 8.0 |
| Slit (nm) | 1.0 |
| LOD (µg L⁻¹) | 0.22 |
| Linear Range (µg L⁻¹) | 0.5-58 |
| Mode | Peak area |

2.3. Sampling

For sampling, the clean glass tubes and container were purchased from Iranian company. The 10 mL of human blood samples were collected from industrial factory of Iran. For sampling, all glass tubes were washed with a 0.5 mol L⁻¹ HNO₃ solution for at least 24 h and thoroughly rinsed 10 times with ultrapure water (UPW) before using. As concentrations of arsenic in blood / serum are very low, even minor contamination at any stage of sampling, sample storage and handling, or analysis has the potential to affect the accuracy of the results. For analysis in blood 10 µL, pure heparin (free metals) is added to a 10 mL blood sample. The human blood sample was maintained at –20 °C in a cleaned glass tube. The water prepared in 250 mL of polyethylene bottle (PEB) based on ASTM for sampling and storage by acidifying.

2.4. General procedure

The developed method based on centrifuging dispersive liquid-liquid microextraction (CD-LLME) was used for arsenic speciation in human blood and water samples at pH=4.5. By proposed procedure, the concentrations of As (III, V) in range of 1-5.8 µg L⁻¹ were determined by HG-AAS in human blood and water samples. As (III) can be extracted with TOMAS in liquid phase without any chelating agent at optimized pH. Flame condition tuned based on 1.2 L min⁻¹ of fuel with low air flowrate for As by HG-AAS. By CD-LLME procedure, 0.12 g of TOMAS diluted with 0.2 mL of acetone and injected into 10 mL of blood and standard samples which was included the arsenic concentration of 1-5.8 µg L⁻¹. Then, the pH was adjusted to 4.5 with buffer solution, shaking for 5 min and then transferred to a centrifuge tube. Arsenic (III) was complexed with TSIL (As-TOMAS) and then, the TSIL were separated from liquid phase by centrifuging of turbid solution at 3 min with 3500 rpm. The upper phase of TOMAS, with olive green color layer, was removed with a transfer pipette to PEB (5 mL). The As(III) was back-extracted from TOMATS at acidic pH by 0.5 mL of hydrochloric acid solution (2 M) which was shaken for 1.0 min and diluted with ultrapure water up to 1mL. Then, the TOMAS phase was removed by centrifuging and pipette and aqueous phase was determined by HG-AAS. The same procedure was done on sample blank for water and human serum/blood samples without As(III,V). Finally, the As (V) was reduced to As (III) with KI (1M) and ascorbic acid, the total arsenic (TAs) was determined. In addition, the concentration of As (V) was calculated by subtracting the content of As (III) from total arsenic content. The extraction conditions based on TOMAS were explained in Table 2.

3. Results and Discussion

In proposed method, for increasing higher sensitivity, selectivity and precision, of determining and speciation arsenic (As) in blood and water samples, we studied and optimized thoroughly, the effect of the main parameters, like the type of disperser and extraction solvent, sample volume, sample acidity, amount of TOMAS as chelating agent, and extraction time. All analyses were carried out in triplicate.
metal hydride is formed and then passed through a gas-liquid separator where the hydride vapor is removed from the bulk liquid using an inert carrier gas. The hydride is then fed into a fused quartz absorption cell. For arsenic determination the cell is mounted over a burner and heated by an air-acetylene flame (HGAAS). Flame conditions were with 1.2 L min\(^{-1}\) fuel and minimum flow air.

### 3.2. Effect of pH range

The complexation phenomenon is strongly conditioned by the pH of solutions and subsequently affects the extraction efficiency of the As(III) by complexing of TOMAS. As previously research, ionic liquids such as TOMAS was decomposed in lower pH (less than pH=3). Therefore, the effect of pH was studied and evaluated in the pH range of 3 – 11 as a lower limit of quantification (LLOQ) and upper limit of quantification (ULOQ) for 0.05-5.0 μg L\(^{-1}\) for As(III). The results show that the high extraction efficiency for As (III) were achieved in pH=4.5 and As(V) had no extraction in optimized pH (less than 5%). So, the procedure was applied to speciation of arsenic in water and blood samples (Fig. 2).

### 3.1. Instrumental

The repeatability of results was investigated for speciation and determination arsenic in blood and water samples by hydride generation atomic absorption spectrometer (HGAAS) in present of flame. After mixing reagents and samples, the mixture solution moved to reaction coil where the

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**Table 2. The extraction conditions of As(III) based on TOMAS by CD-LLME method**

| Features (Human blood)          | Value As | Features (Water)          | Value As |
|---------------------------------|----------|---------------------------|----------|
| Mean RSD% (blood, n=10)         | 3.2      | Mean RSD% (water, n=10)   | 2.8      |
| LOD of CD-LLME(blood, μg L\(^{-1}\)) | 0.022    | LOD of CD-LLME(water, μg L\(^{-1}\)) | 0.004    |
| Enrichment factor(blood)        | 9.8      | Enrichment factor(water)   | 48.6     |
| Volume of blood (mL)            | 10       | Volume of water(mL)        | 50       |
| Linear range of blood, PA (μgL\(^{-1}\)) | 0.05 –5.9 | Linear range of water, PA (μgL\(^{-1}\)) | 0.01-1.1 |
| Correlation coefficient of DLLME| R = 0.9965 | Correlation coefficient of DLLME | R = 0.9983 |

PA = Peak Area

**Fig. 2.** The effect of pH on As(III) extraction based on TOMAS by CD-LLME method
3.3. Optimization of amount of TSIL and extraction time

The variation of extraction efficiency upon TOMAS amount as TSIL was examined within the range of 0.02-0.2 g for arsenic concentration from 0.05 to 5.0 μg L⁻¹ in blood samples. It was observed that the extraction efficiency of the system was remarkably affected by the TSIL amount. Quantitative extraction of As(III) based on TOMAS was observed more than 0.08 g and 0.1 g for 10 mL and 50 mL of blood and water samples, respectively. So, 0.12 g of TOMAS was selected as optimum amount of TSIL for arsenic speciation in both samples (Fig.3). Triton X-100, an emulsifier and anti-sticking agent, was added to the solution in order to raise the efficiency of the extraction procedure. After added TX-100 [1% (w/v)] the quantitative extraction was observed for arsenic by TOMAS in human blood samples.

The effectiveness of As(III) extraction under the influence of shaking and centrifugation time was studied. The different shaking and centrifuging times (3500rpm) were studied and optimized by CD-LLME procedure. The results showed us, the 5.0 min of shaking and 3.0 min of centrifuging had efficient extraction for proposed method.

3.4. Effect of sample volume

Sample volume is one of the most important parameter to be studied when real samples are analyzed by a pre-concentration technique, since it conditions the sensitivity enhancement of the method. The effect of sample volume was examined in a range of 1–100 mL for 5.0 μg L⁻¹ and 1.0 μg L⁻¹ As(III) ions in blood and water samples, respectively. It was found that the As(III) could be quantitatively extracted in blood samples for 12 mL of the sample solution. At higher a volume the recoveries are decreased. It was also noticed that higher sample volumes partially solubilized the TOMAS in liquid phase and lead to non-reproducible results. Therefore sample volume of 10 mL was selected for further experiments for human blood samples. Also, the results showed, the As(III) was efficient extracted based on TOMAS in 60 mL of water samples. So, 50 mL of water samples selected for further study (Fig. 4).

![Fig. 3. The effect of amount of TOMAS on As(III) extraction by CD-LLME method](image-url)
3.5. Interferences study.
TOMAS is a TSIL with thiol (HS) group which was acted as a chelating agent for many transition metals. Thus, for extraction of As(III) with TOMAS, the interferences coexisting ions such as mercury, lead, copper, zinc, vanadium, and silver should be considered. The effect of potential interfere occurring in blood and water samples on the determination of As(III) were tested in optimized conditions by CD-LLME procedure. The extraction recovery of TOMAS for 0.05-5.9 μg L\(^{-1}\) and 0.01-1.0 μg L\(^{-1}\) of As(III,V) was tested in blood and water samples with individual ions interferences. The results showed that many ions could be tolerated up to at least 1-3 mg L\(^{-1}\). Mercury and silver had low tolerated up to at least 80-400 μg L\(^{-1}\) by using TOMAS in water and blood samples. High concentrations of alkali metals, alkaline earth metals, CO\(_3^{2-}\) and PO\(_4^{3-}\) which are usually found in blood samples, were tested by 0.5-1.0 mg L\(^{-1}\) and did not effect on extraction recovery of As(III) by CD-LLME procedure (Table 3).

3.6. Method validation
For validation of proposed method, 10 mL and

![Fig. 4. The effect of sample volume for As(III) extraction by CD-LLME method](image)

Table 3. The effect of interferences coexisting ions on extraction of As(III) in human blood and water samples by CD-LLME method

| Interfering Ions in blood(M) | Mean ratio \(\frac{C_M}{C_{As(III)}}\) | Recovery (%) |
|-----------------------------|-------------------------------|-------------|
| As(III)                     | As(III)                       |             |
| Cr\(^{3+}\), Al\(^{3+}\), Mn\(^{2+}\), Cd\(^{2+}\), V\(^{3+}\), Pb\(^{2+}\) | 750               | 98.8        |
| Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Mo\(^{2+}\) | 500               | 95.9        |
| I\(^{-}\), Br\(^{-}\), F\(^{-}\), Cl\(^{-}\) | 1000              | 98.5        |
| Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\) | 900               | 99.1        |
| CO\(_3^{2-}\), PO\(_4^{3-}\), HCO\(_3^{-}\) | 700               | 96.7        |
| Ag\(^{+}\)                  | 300              | 98.2        |
| Hg\(^{2+}\)                 | 80               | 96.6        |
| NO\(_3^{-}\), SO\(_4^{2-}\) | 800              | 97.5        |

| Interfering Ions in water (M) | Mean ratio \(\frac{C_M}{C_{As(III)}}\) | Recovery (%) |
|------------------------------|-------------------------------|-------------|
| As(III)                      | As(III)                       |             |
| Cr\(^{3+}\), Al\(^{3+}\), Mn\(^{2+}\), Cd\(^{2+}\), V\(^{3+}\), Pb\(^{2+}\) | 900               | 97.7        |
| Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Mo\(^{2+}\) | 650               | 97.2        |
| I\(^{-}\), Br\(^{-}\), F\(^{-}\), Cl\(^{-}\) | 1200              | 97.4        |
| Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\) | 1000              | 98.6        |
| CO\(_3^{2-}\), PO\(_4^{3-}\), HCO\(_3^{-}\) | 950               | 96.6        |
| Ag\(^{+}\)                  | 400              | 99.2        |
| Hg\(^{2+}\)                 | 150              | 97.3        |
| NO\(_3^{-}\), SO\(_4^{2-}\) | 1000             | 98.1        |
50 mL of blood and water samples were used. Results showed that there are no interferences from major consistent of blood samples, therefore we have explored the feasibility of the methodology using proposed method for the determination of As(III) ions in different matrices. Validation of the methodology was performed by standard reference material (NIST SRM 2670) with certified values for arsenic speciation (Table 4). Also, the spiked of standard arsenic solutions with real human blood and water samples were done to demonstrate the reliability of the method for determination and speciation of As (III) and As (V) (Table 5). In addition, the ability of different methods compared to CD-LLME method in Table 6. The TOMAS based on CD-LLME-HGAAS technique can be used for determination and speciation of arsenic (As⁺, As⁺⁺) in human samples as compared to HG-AAS or ET-AAS.

3.7. Comparing to other methods

The figures of merit of the CD-LLME method compared to the alternative methods for arsenic speciation (III, V) in different matrices (Table 7). Recently, the different techniques for extraction/separation/determination arsenic species in human biological fluids and waters have been reported. Some techniques such as dispersive liquid–liquid microextraction (DLLME), cloud point extraction, and solid phase extraction have already used for extraction and speciation arsenic [18-21]. In this work, the TSIL (TOMAS) based CD-LLME combined with CV-AAS for speciation and determination of As (II, V) in human blood and water samples. The LOD, RSD and linear range values compared to other published method. Wen et al. used cloud point extraction with ICP-optical emission spectrometry for speciation of AS (III, V) with LOD of 0.72 and RSD of 3.5 which was higher than CD-LLME procedure [18]. Based on

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Table 4. Validation of the methodology was performed by standard reference material (NIST SRM 2670)

| SRM     | As(III) | As(V) | Found a As(III) | Found a As(V) | Recovery As(III) | Recovery As(V) |
|---------|---------|-------|-----------------|--------------|-----------------|---------------|
| Urine b | 2.50 ± 0.2 | 1.50 ± 0.2 | 2.52 ± 0.18 | 1.45 ± 0.11 | 100.8 % | 96.6% |
| Blood c | 2.07 ± 0.63 | --- | 1.98 ± 0.12 | --- | 95.7% | --- |

*a Mean value ± standard deviation based on three replicate measurements
*b NIST, SRM 2670, arsenic in frozen dried urine, pH 4.0, -20°C
*c NIST, SRM 955c, Caprine Blood, Level 1

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Table 5. Evaluation of accuracy and precision of results in human blood and water samples by spiking of arsenic standard (III, V) based on CD-LLME method

| Sample | Added | Found a | Recovery (%) |
|--------|-------|---------|--------------|
| CRM*   |       | 2.45 ± 0.14 | 3.87 ± 0.21 | 98.0 | 94.6 | 96.7 |
| 2.0    | 4.41 ± 0.23 | 5.85 ± 0.28 | 98.1 | --- | 99.0 |
| 1.5    | 2.43 ± 0.15 | 2.95 ± 0.16 | 5.38 ± 0.25 | 102 | 100.6 |
| Water  |       | 0.88 ± 0.04 | 1.47 ± 0.07 | --- | --- | --- |
| 1.0    | 1.85 ± 0.09 | 2.46 ± 0.13 | 97.0 | --- | 98.8 |
| 0.5    | 0.87 ± 0.05 | 1.94 ± 0.11 | 95.7 | 94.5 |
| Blood  |       | 1.77 ± 0.08 | ND | 1.77 ± 0.08 | --- | --- |
| 1.5    | 3.24 ± 0.14 | ND | 3.24 ± 0.14 | 98.0 | 98.0 |
| 1.5    | 1.74 ± 0.08 | 1.48 ± 0.07 | 3.22 ± 0.18 | 98.6 | 96.5 |
| Urine  |       | 1.15 ± 0.06 | 2.21 ± 0.11 | --- | --- | --- |
| 1.0    | 2.17 ± 0.08 | 3.19 ± 0.15 | 102 | --- | 97.9 |
| 1.0    | 1.13 ± 0.05 | 3.16 ± 0.16 | 97.0 | 95.0 |

*a Mean value ± standard deviation based on three replicate measurements
*b NIST SRM 2670, arsenic in frozen dried urine, pH 4.5-20°C
Table 6. Comparing of different techniques with CD-LLME method for determination and speciation of arsenic (III, V) in real samples

| As species | Sample | HG-AAS* | CD-LLME/HG-AAS* | LC-MS/MS* |
|------------|--------|---------|----------------|-----------|
| Water      | As (V) | 0.304 ± 0.016 | 0.296 ± 0.012 |
|            | As (III) | 0.197 ± 0.011 | 0.201 ± 0.008 |
|            | Total       | ± 0.027 ± 0.485 | ± 0.024 ± 0.501 ± 0.015 ± 0.497 |
| Blood      | As(V)       | 0.865 ± 0.043 | 0.844 ± 0.032  |
|            | As (III)    | 2.641 ± 0.127 | 2.702 ± 0.096  |
|            | Total      | 3.317 ± 0.175 | 3.486 ± 0.166 | 3.546 ± 0.121 |

*Mean value ± standard deviation based on three replicate measurements (N=5, P= 0.95)

Table 7. Comparison of the published methods with the proposed method in this work

| Method     | Separation | Matrixes | LR* | DL* | RSD% | References |
|------------|------------|----------|-----|-----|------|------------|
| ICP-OES a | APDC-CPE b | Snow water | 2-50 | 0.72 | 3.5 | [18]       |
| ETAAS      | HF-LPME c  | Hair water | 1-50 | 0.12 | 8.0 | [19]       |
| LC-HG-AFS b | 1-octyl-3-methylimidazolium chloride(IL) | Wine | 1-2000 | 0.81 | 2.98 | [20]       |
| ET-AAS     | DDTP-CLLME h | Plasma urine | 0.1-50 | 0.03-0.05 | 4.0-5.7 | [21]       |
| HGAAS      | TOMAS-CD-LLME | Blood | 0.05 – 5.9 | 0.022 | 3.2 | This work |
| HGAAS      | TOMAS/CD-LLME | Water | 0.01 –1.1 | 0.004 | 2.8 | This work |

*Linear range (LR, μg L−1); Detection limit (DL, μg L−1)

a ICP-OES = Inductively coupled plasma-optical emission spectrometry
b APDC-CPE = Ammonium 1-pyrrolidinedithiocarbamate (APDC) - Cloud point extraction (CPE)
c HF-LPME = Hollow fiber liquid phase microextraction combined
d LC-HG-AFS = Liquid chromatography - hydride generation atomic fluorescence spectrometry
h DDTP-CLLME = Diethyldithiophosphoric acid (DDTP)-Centrifuging liquid-liquid microextraction

Table 7, the sensitivity of the developed method is similar to other reported methods. The linear range was perfectly adequate for the analyzed human blood samples. Lower LOD values are related with higher sensitivity of proposed method which was used in this study. Also, some methods have higher PF that analyzed by ICP in water or human blood samples with large sample volume. TSIL (TOMAS) based CD-LLME combined with CV-AAS showed a rapid and easy extraction and speciation of As (III,V) using a user-friendly instruments.

4. Conclusions

The procedure here studied takes advantage of the combination of a very simple, reliable way of pre-concentrating in sea water and blood samples for arsenic determination and speciation with the sensitive TOMAS@HG-AAS technique. The increase in sensitivity resulting of sample pre-concentration, good sample frequency and possibility of speciation of As (III), As (V) forms of these analytes, means the procedure can be considered an alternative to high-performance liquid chromatography (HPLC) in combination with inductively coupled plasma mass spectrometry (ICP-MS), Ion Chromatography Coupled to inductively coupled plasma mass spectrometry (IC-ICP-MS) and ICP-MS. The results showed that the quantitative extraction (QE) and enrichment factor (EF) for water samples were more than 95% and 49.6, respectively (RSD<5%). Linear range of arsenic in blood and water samples was obtained 0.05 –5.9 and 0.01-1.1μgL−1, respectively by CD-LLME method. By proposed procedures, the satisfactory results of ultra-trace analysis for arsenic species in blood and water samples were achieved.

5. Acknowledgements

The authors thank from Semnan University and
Research Institute of Petroleum Industry (IRPI), Tehran, Iran.

6. References

[1] A.T. Townsend, K.A. Miller, S. McLean, S. Aldous, The determination of copper, zinc, cadmium and lead in urine by high resolution ICP-MS, J. Anal. Atom. Spec., 13 (1998) 1213-1219.

[2] J.S. Petrick, F. Ayala-Fierro, W.R. Cullen, D.E. Carter, H.V. Aposhian, Monomethylarsonous acid (MMAIII) is more toxic than arsenite in Chang human hepatocytes, Toxicol. Appl. Pharm., 163 (2000) 203-207.

[3] X. Zhang, R. Cornelis, J. de Kimpe, L. Mees, Speciation of toxicologically important arsenic species in human serum by liquid chromatography–hydride generation atomic absorption spectrometry, J. Anal. Atom. Spec., 11 (1996) 1075-1079.

[4] H. Shirkhanloo, A. Rouhollahi, H.Z. Mousavi, Ultra-trace arsenic determination in urine and whole blood samples by flow injection-hydride generation atomic absorption spectrometry after preconcentration and speciation based on dispersive liquid-liquid microextraction, Bull. Korean Chem. Soc., 32 (2011) 3923-3927.

[5] A. Hussam, M. Alauddin, A. Khan, S. Rasul, A. Munir, Evaluation of arsine generation in arsenic field kit, Environ. Sci. Technol., 33 (1999) 3686-3688.

[6] M. Van Hulle, C. Zhang, X. Zhang, R. Cornelis, Arsenic speciation in chinese seaweeds using HPLC-ICP-MS and HPLC-ES-MS, Analyst, 127 (2002) 634-640.

[7] X. Li, B.J. Coles, M.H. Ramsey, I. Thornton, Sequential extraction of soils for multielement analysis by ICP-AES, Chem. Geology, 124 (1995) 109-123.

[8] A. Shraim, B. Chiswell, H. Olszowy, Speciation of arsenic by hydride generation–atomic absorption spectrometry (HG–AAS) in hydrochloric acid reaction medium, Talanta, 50 (1999) 1109-1127.

[9] J.T. van Elteren, Z. Šlejkovec, M. Svetina, A. Glinšek, Determination of ultratrace dissolved arsenite in water–selective coprecipitation in the field combined with HGAFS and ICP-MS measurement in the laboratory, Fresenius’ j. Anal. Chem., 370 (2001) 408-412.

[10] F. Shemirani, M. Baghdadi, M. Ramezani, M.R. Jamali, Determination of ultra trace amounts of bismuth in biological and water samples by electrothermal atomic absorption spectrometry (ET-AAS) after cloud point extraction, Anal. Chim. Acta, 534 (2005) 163-169.

[11] S. Smirnova, T. Samarina, I. Pletnev, Hydrophobic–hydrophilic ionic liquids for the extraction and determination of metal ions with water-soluble reagents, Anal. Method., 7 (2015) 9629-9635.

[12] A.A. Miranbeigi, M. Yousefi, M. Abdouss, Room temperature imidazolium-based ionic liquids as scavengers for hydrogen sulfide removal of crude oil, Anal. Method. Environ. Chem. J., 1 (2018) 11-22.

[13] S. Davari, F. Hosseini, H. Shirkhanloo, Dispersive solid phase microextraction based on aminefunctionalized bimodal mesoporous silica nanoparticles for separation and determination of calcium ions in chronic kidney disease, Anal. Method. Environ. Chem. J., 1 (2018) 57-66.

[14] A. Khaligh, H. Shirkhanloo, Food Analysis: Task specific ionic liquids for separation of nickel and cadmium from olive oil samples by thermal ultrasound-assisted dispersive multiphasic microextraction, Anal. Method. Environ. Chem. J., 2 (2019) 55-64.

[15] M. Chamsaz, M.H. Arbab-Zavar, S. Nazari, Determination of arsenic by electrothermal atomic absorption spectrometry using headspace liquid phase microextraction after in situ hydride generation, J. Anal. Atom. Spec., 18 (2003) 1279-1282.

[16] J. Ping, J. Wu, Y. Ying, M. Wang, G. Liu, M. Zhang, Evaluation of trace heavy metal levels in soil samples using an ionic liquid modified carbon paste electrode, J. Agri. food Chem., 59 (2011) 4418-4423.

[17] M. Gharehbaghi, F. Shemirani, Ionic liquid modified silica sorbent for simultaneous separation and preconcentration of heavy metals from water and tobacco samples prior to their determination by flame atomic absorption spectrometry, Anal. Method., 4 (2012) 2879-2886.

[18] S. Wen, X. Zhu, Speciation of inorganic As(III) and As(V) by a facile dual-cloud point extraction coupled with inductively plasma-optical emission spectrometry, Talanta 181(2018) 265-270.

[19] H. Jiang, B. Hu, B. Chen, L. Xia, Hollow fiber
liquid phase microextraction combined with electrothermal atomic absorption spectrometry for the speciation of arsenic (III) and arsenic (V) in fresh waters and human hair extracts, Anal. Chim. Acta 634 (2009) 15-21.

[20] A. Castro Grijalba, E.F. Fiorentini, L.D. Martinez, R.G. Wuilloud, A comparative evaluation of different ionic liquids for arsenic species separation and determination in wine varietals by liquid chromatography - hydride generation atomic fluorescence spectrometry, J. Chromatogr. A 1462 (2016) 44-54.

[21] L. Haghnaazi, N. Mirzaei, H. Arfaeinia, K. Karimyan, H. Sharaﬁ, N. Fattahi, Speciation of As(III)/As(V) and total inorganic arsenic in biological fluids using new mode of liquid-phase microextraction and electrothermal atomic absorption spectrometry, Biol. Trace Elem. Res., 183 (2018) 173–181.