



Optimized ultrasound-assisted emulsification microextraction for simultaneous trace multielement determination of heavy metals in real water samples by ICP-OES

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ABSTRACT

Ultrasonic-assisted emulsification microextraction (USAEME) combined with inductively coupled plasma-optical emission spectrometry (ICP-OES) was used for preconcentration and determination of aluminum, bismuth, cadmium, cobalt, copper, iron, gallium, indium, nickel, lead, thallium and zinc in real water samples. Ammonium pyrrolidine dithiocarbamate (APDC) and carbon tetrachloride (CCl₄) were used as the chelating agent and extraction solvent, respectively. The effective parameters (factors) of the extraction process such as volume of extraction solvent, pH, sonication time, and concentration of chelating agent were optimized by a small central composite design (CCD). The optimum conditions were found to be 98 μL for extraction solvent, 1476 mg L^{-1} for chelating agent, 3.8 for pH and 9 min for sonication time. Under the optimal conditions, the limits of detection (LODs) for Al, Bi, Cd, Co, Cu, Fe, Ga, In, Ni, Pb, Tl and Zn were 0.13, 0.48, 0.19, 0.28, 0.29, 0.27, 0.27, 0.38, 0.44, 0.47, 0.52 and 0.17 $\mu\text{g L}^{-1}$, respectively. The linear dynamic range (LDR) was 1–1000 $\mu\text{g L}^{-1}$ with determination coefficients of 0.991–0.998. Relative standard deviations (RSDs, $C=200 \mu\text{g L}^{-1}$, $n=6$) were between 1.87%–5.65%. The proposed method was successfully applied to the extraction and determination of heavy metals in real water samples and the satisfactory relative recoveries (90.3%–105.5%) were obtained.

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1. Introduction

Heavy metals are the elements that naturally found in the earth's crust. Excessive levels of heavy metals can be introduced into the environment as a consequence of human activities and rapid industrialization. The trace amounts of some heavy metals are essential to the human body. However, at higher concentrations they can be dangerous and seriously damaging the human health. They are non-biodegradable and can be accumulated in living tissues, causing various diseases and disorders. Therefore, determination of trace levels of heavy metals is very critical in the context of environmental protection, food and agricultural chemistry and also for monitoring environmental pollution [1–3].

Several atomic spectrometric techniques such as flame atomic absorption spectrometry (FAAS) [3], electrothermal atomic absorption spectrometry (ETAAS) [4] inductively coupled plasma-mass spectrometry (ICP-MS) [5] and inductively coupled plasma-optical emission spectroscopy (ICP-OES) [6] have been widely used for determination of trace amounts of heavy metal ions in environmental samples. ICP-OES offers fast multi-elemental simultaneous

analysis resulting in a wide range of applications including complex and organic matrices with an extended dynamic range and robust matrix tolerance. Since the samples experience inert and high temperatures medium, even the most refractory elements are atomized and excited very efficiently with relatively low interference effects. The limits of detection for the refractory elements can be well over an order of magnitude better than the corresponding values for atomic absorption. However, due to insufficient sensitivity and matrix interferences, direct determination of the metal ions at trace levels, by this technique, is limited. Therefore, a separation and/or a pre-concentration step prior to the analysis are necessary [6].

Various sample preparation methods including solid-phase microextraction (SPME) [7], head space single-drop microextraction (HS-SDME) [8], liquid phase microextraction (LPME) [9], hollow fiber liquid phase microextraction (HF-LPME) [5], hollow fiber supported liquid membrane extraction (HF-SLME) [10], on-line ionic liquid (IL) dispersive microextraction [11] and dispersive liquid-liquid microextraction (DLLME) [12–15] have been developed for this purpose.

Moreover, the extraction methods involving ultrasound such as ultrasound-assisted emulsification microextraction (USAEME) for pretreatment of water samples followed by multi-elemental analysis were also developed [16–19]. USAEME method is a

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combination of microextraction systems and ultrasound that provides an efficient preconcentration technique. This technique is low cost, simple and fast that increases the contact surface area between the extraction solvent and the analyte solution at room temperature without using a disperser solvent.

In this work, a response surface methodology optimized-USAEME followed by ICP-OES was developed and applied to simultaneous trace multielement preconcentration and determination of twelve heavy metal ions in real water samples. APDC was used as the chelating agent and carbon tetrachloride (CCl_4) was selected as the extraction solvent. The important operating variables of the extraction were optimized using an experimental design approach. To demonstrate the applicability of this method, the optimized procedure was employed to determine heavy metals in various real samples.

2. Experimental

2.1. Apparatus

A Vista-MPX ICP-OES (Varian Inc., Melbourne, Victoria 3170, Australia) equipped with a slurry nebulizer and a charge coupled device detector was used for simultaneous determination of the analytes. The instrument parameters and the most sensitive and interference-free emission lines of each element are shown in Table 1. A 100 μL Hamilton syringe (Bonaduz, Switzerland) was used to inject organic solvent into aqueous sample solutions. A Metrohm 691 pH meter (CH-9100 Herisau, Switzerland) with a combined glass electrode was used for the pH measurements. Centrifuges were performed by a Hermel-Z 200 A (Wehingen-Germany). An Eurosonic 4D (Euronda, Montecchio Precalcino (Vincenza) Italy) ultrasonic water bath with a temperature control and a digital timer was used to emulsify the extraction solvent.

2.2. Reagents and materials

Carbon tetrachloride, trichloroethylene, tetrachloroethylene, chloroform, potassium dihydrogen phosphate, potassium hydrogen phthalate, stock standard solutions of Al, Bi, Cd, Co, Cu, Fe, Ga, In, Ni, Pb, Tl and Zn (1000 mg L^{-1}) with the purity higher than 99% and HNO_3 (65%, extra pure) were purchased from Merck Chemicals (Darmstadt, Germany). The standard solutions were diluted with double distilled water to prepare the mixed standard solutions. Working solutions were prepared daily by appropriate dilution of the mixed standard solutions. The pH value of the solutions was adjusted by dissolving proper amount of potassium hydrogen phthalate (0.1 M) and potassium dihydrogen phosphate in water (0.1 M) and dropwise addition of 1 M sodium hydroxide solutions and/or 1 M nitric acid. The laboratory glassware was kept for 24 h in a 1 M HNO_3 solution and subsequently washed with double distilled water before use. Water standard reference

material of CRM-TMDW-500 drinking water (High-Purity Standards Inc., Charleston, SC, USA) and river water reference material NRCC-SLRS-4 (National Research Council of Canada, Ottawa, Ontario, Canada) were employed for validation of the proposed method.

2.3. Preconcentration procedure

10.0 mL of the buffered solution (pH 3.8) containing $200 \mu\text{g L}^{-1}$ of Al, Bi, Cd, Co, Cu, Fe, Ga, In, Ni, Pb, Tl and Zn was placed in a 12 mL screw cap glass test tube with conic bottom. Then, 1.0 mL of APDC solution (1476 mg L^{-1}) was added to it. The tube was then placed into the ultrasonic water bath. At this stage, 98 μL of CCl_4 (extraction solvent) was slowly injected into the sample solution by using a 100 μL Hamilton syringe. In this step, metal ions reacted with APDC to form related complexes. A cloudy solution (water and fine droplets of carbon tetrachloride) was formed. The extraction was completed under ultrasound in 9 min at the laboratory temperature ($\sim 25^\circ\text{C}$). Then, the emulsion was disrupted by centrifugation at 5000 rpm for 2 min and thus the organic phase was sedimented at the bottom of the tube. The sedimented phase was completely removed and transferred to another test tube and dried at 70°C in an oven. Finally, the residue was dissolved into 0.5 mL 1 M HNO_3 and was analyzed by ICP-OES.

3. Results and discussion

APDC is the most widely used chelating agent that efficiently extracts a large number of metals over a pH range from water samples. The extraction in the proposed method was based on the metal-APDC chelates formation and the subsequent extraction into CCl_4 by the aid of ultrasound. The ultrasound was used as an emulsifier to disperse the fine droplets of the extraction solvent into the water sample without addition of a disperser solvent. The preconcentrated analytes were determined simultaneously by ICP-OES. To achieve a high extraction recovery (ER) and enrichment factor (EF), the significant factors (parameters) were optimized by using a central composite design. The average extraction recovery (ER) of the analytes was considered as “experimental response” to evaluate the method performance. ER was defined as follows:

$$ER = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 \quad (1)$$

where C_{sed} is concentration of the analyte in the sedimented phase, C_0 is the initial concentration of analyte in the sample solution; V_{sed} and V_{aq} are the volumes of sedimented and sample solutions, respectively. The enrichment factor was calculated by using Eq. (2).

$$EF = \frac{C_{sed}}{C_0} \quad (2)$$

3.1. Selection of extraction solvent

The solvents with higher density than water, immiscibility with water, good solubility toward the chelate of the analytes and forming a stable emulsion system were considered for the extraction. Carbon tetrachloride (density: 1.59 g mL^{-1}), tetrachloroethylene (density: 1.62 g mL^{-1}) chloroform (density: 1.48 g mL^{-1}) and trichloroethylene (density: 1.46 g mL^{-1}) were examined. The extraction was performed with 100 μL of each solvent, then emulsified in a 10 mL of aqueous sample containing

Table 1
Instrumental parameters of ICP-OES and metal ions emission lines.

| Parameter | Value |
|---|---|
| RF generator power (kW) | 1.3 |
| Plasma gas flow rate (L min^{-1}) | 15 |
| Auxiliary gas flow rate (L min^{-1}) | 1.5 |
| Nebulizer pressure (kPa) | 150 |
| Torch mode | axial |
| Analytical lines (nm) | Al (396), Bi (223), Cd(214) Co(238), Cu (327), Fe(259) Ga (417), In (325), Ni(216) Pb (220), Tl (276) Zn (213) |

200 $\mu\text{g L}^{-1}$ of each element. The results in Fig. 1 show that the highest extraction efficiency was obtained with carbon tetrachloride. The recovery of the analytes was 50% for Al, 88% for Bi, 88% for Cd, 85% for Co, 84% for Cu, 76% for Fe, 81% for Ga, 89% for In, 77% for Ni, 86% for Pb, 32% for Tl and 95% for Zn (with the average recovery of $\sim 78\%$). Therefore, it was selected as the extraction solvent.

3.2. Optimization of the USAEME process: central composite design

To improve the performance of the method and obtaining the conditions at which the procedure produces the best possible response, a rotatable central composite design (CCD) was employed. Rotatability provides constant variance of the estimated response corresponding to all new observation points that are at the same distance from the center point of the design [20]. To reduce the number of the experiments for optimization a small CCD was planned. It contained an imbedded half-fraction factorial design ($N_f=2^{f-1}$) with a set of center points (N_0) that is augmented with a group of “star points” ($N_a=2f$) that allow estimation of curvature. Here, f is the number of the factors under investigation. Based on our preliminary studies and experiments, volume of extraction solvent, pH, sonication time and concentration of chelating agent were recognized as the main parameters of USAEME. Therefore, f is equal to four. The repetition of the experiments at the center (middle) points of the parameters usually gives a good estimate of experimental error (pure error). The star points are located at $+\alpha$ and $-\alpha$ from the center of the experimental domain. The value of “ α ” needed to ensure the rotatability was obtained from the following equation equal to ± 1.682 .

$$\alpha = \sqrt[4]{N_f} \quad (3)$$

The total number of experiments required (N) to run the CCD was calculated by using Eq. (4) equal to 22.

$$N = N_f + N_a + N_0 \quad (4)$$

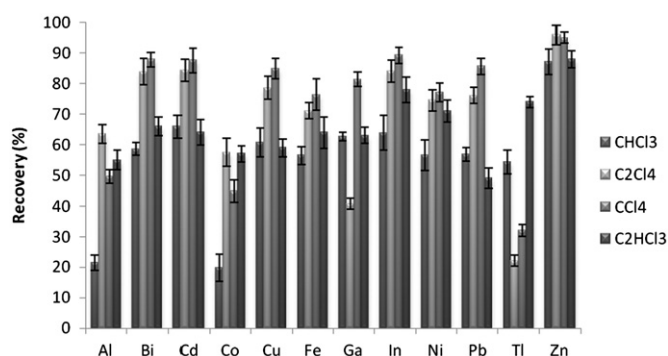


Fig. 1. Effect of type of extraction solvent on the extraction recovery of the analytes. Extraction condition: sample volume, 10 mL; volume of extraction solvent, 98 μL ; pH, 3.8; sonication time, 9 min; concentration of the analytes, 200 $\mu\text{g L}^{-1}$; concentration of chelating agent, 1476 mg L^{-1} .

Table 2

Factors, their symbols and levels for the central composite design.

| Factor | Symbol | Level | | | | |
|---|--------|-----------|------|------|------|-----------|
| | | $-\alpha$ | -1 | 0 | 1 | $+\alpha$ |
| Volume of extraction solvent (μL) | E | 30 | 48 | 75 | 100 | 120 |
| pH | P | 3 | 4 | 5 | 6 | 7 |
| Concentration of chelating agent (mg L^{-1}) | L | 400 | 684 | 1100 | 1516 | 1800 |
| Ultrasonic time (min) | t | 5 | 7 | 10 | 13 | 15 |

The experiments were randomized in order to minimize the effect of uncontrolled factors. As it was not possible to carry out the experiments during a working day, they were divided into two blocks and carried out in two sequential days to remove the expected variations caused by some changes during the course of the experiments [21]. The main factors, their symbols and levels are given in Table 2. The experimental design matrix that is consisted of the number and order of the experiments, levels of the factors in each experiment and the related responses (extraction recoveries) is shown in Table 3.

To evaluate the significance of the model equation and the related terms, analysis of variance (ANOVA) was considered (Table 4). The F-values indicate that the model is significant and the lack of fit is not significantly relative to the pure error, hence confirm the validity of the model. Significant effects should have “probe > F” values less than 0.0500. In this case, E , t , EP , PL , E^2 , L^2 , P^2 and t^2 were the significant effects. A second order polynomial with the most reasonable statistics, were considered as the satisfactory response surface model to fit the experimental data. This model that is shown in Eq. (5) consists of four main effects (E , P , L and t), two two-factor interaction effects (EP and PL), and four curvature effects (E^2 , P^2 , L^2 and t^2) as follows:

$$Y = b_0 + b_1E + b_2P + b_3L + b_4t + b_5EP + b_6PL + b_7E^2 + b_8P^2 + b_9L^2 + b_{10}t^2$$

$$b_0 = 87.9; b_1 = 3.3; b_2 = -2.9; b_3 = 0.2; b_4 = -5.3;$$

$$b_5 = -10.9; b_6 = -10.3;$$

$$b_7 = -7.5; b_8 = -9.6; b_9 = -6.4; b_{10} = -7.1. \quad (5)$$

where Y is the response (extraction recovery), b_0 is the intercept and the other b terms (b_1 – b_{10}) are the coefficients. The sign of a coefficient (+ or –) defines the direction of relationship between the related effect and the response. The positive sign indicates that as the value of one effect changes, the value of the response changes in the same direction too, while for the negative sign the response operates in the opposite direction. The absolute value of the coefficients measures the strength of the relationship.

The quality of the polynomial model was expressed by the coefficient of determination (R^2 , adjusted- R^2 and adequate precision). R^2 is a measure of the amount of variations around the mean explained by the model and it is equal to 0.9423. The adjusted- R^2 is adjusted for the number of terms in the model and it decreases as the number of terms in the model increases, if those additional terms do not add value to the model. It is equal to 0.8846. Adequate precision is a signal-to-noise ratio. It compares the range of the predicted values at the design points to the average prediction error (Eq. (6)). Ratios greater than 4 indicate adequate model discrimination. Here, it is equal to 11.405.

$$\left[\frac{\max(\hat{Y}) - \min(\hat{Y})}{\sqrt{\bar{V}(\hat{Y})}} \right] > 4, \quad \bar{V}(\hat{Y}) = \frac{1}{n} \sum_{i=1}^n V(\hat{Y}) = \frac{p\sigma^2}{n} \quad (6)$$

\hat{Y} is the predicted value, p is the number of model parameters (including intercept (b_0) and any block coefficients), σ^2 = residual MS from ANOVA table, and n is the number of experiments.

Table 3
Design matrix and responses for the central composite design.

| Run | Block | E | P | L | t | Recovery ^a (%) |
|-----|-------|-----|---|------|----|---------------------------|
| 1 | 1 | 75 | 5 | 1100 | 10 | 91 |
| 2 | 1 | 100 | 6 | 1516 | 7 | 49 |
| 3 | 1 | 100 | 4 | 684 | 13 | 70 |
| 4 | 1 | 100 | 6 | 684 | 7 | 69 |
| 5 | 1 | 75 | 5 | 1100 | 10 | 93 |
| 6 | 1 | 75 | 5 | 1100 | 10 | 88 |
| 7 | 1 | 48 | 4 | 1516 | 7 | 70 |
| 8 | 1 | 100 | 4 | 1516 | 13 | 77 |
| 9 | 1 | 48 | 6 | 1516 | 13 | 49 |
| 10 | 1 | 75 | 5 | 1100 | 10 | 86 |
| 11 | 1 | 48 | 6 | 684 | 13 | 71 |
| 12 | 1 | 48 | 4 | 684 | 7 | 50 |
| 13 | 2 | 75 | 3 | 1100 | 10 | 60 |
| 14 | 2 | 75 | 5 | 1100 | 15 | 56 |
| 15 | 2 | 30 | 5 | 1100 | 10 | 57 |
| 16 | 2 | 75 | 7 | 1100 | 10 | 56 |
| 17 | 2 | 120 | 5 | 1100 | 10 | 71 |
| 18 | 2 | 75 | 5 | 1100 | 5 | 74 |
| 19 | 2 | 75 | 5 | 1100 | 10 | 92 |
| 20 | 2 | 75 | 5 | 400 | 10 | 62 |
| 21 | 2 | 75 | 5 | 1100 | 10 | 83 |
| 22 | 2 | 75 | 5 | 1800 | 10 | 72 |

^a The average extraction recovery of the analytes.

Table 4
Analysis of variance (ANOVA) for the central composite design.

| Source | Sum of squares | d.f. ^a | Mean square | F-value ^b | p-value, prob > F ^c | |
|------------------------|----------------|-------------------|-------------|----------------------|--------------------------------|-----------------|
| Block | 70.63 | 1 | 70.63 | 2.90 | 0.1194 | Not significant |
| Model | 3978.54 | 10 | 397.85 | 16.33 | < 0.0001 | Significant |
| E | 139.87 | 1 | 139.87 | 5.74 | 0.0376 | Significant |
| P | 96.96 | 1 | 96.96 | 3.98 | 0.0740 | Not significant |
| L | 0.41 | 1 | 0.41 | 0.02 | 0.8999 | Not significant |
| t | 157.34 | 1 | 157.34 | 6.46 | 0.0293 | Significant |
| EP | 261.82 | 1 | 261.82 | 10.75 | 0.0083 | Significant |
| PL | 600.73 | 1 | 600.73 | 24.66 | 0.0006 | Significant |
| E ² | 834.67 | 1 | 834.67 | 34.26 | 0.0002 | Significant |
| P ² | 1269.16 | 1 | 1269.16 | 52.09 | < 0.0001 | Significant |
| L ² | 619.60 | 1 | 619.60 | 25.43 | 0.0005 | Significant |
| t ² | 769.80 | 1 | 769.80 | 31.60 | 0.0002 | Significant |
| Residual | 243.64 | 10 | 24.36 | | | |
| Lack of Fit | 174.14 | 6 | 29.02 | 1.67 | 0.3224 | Not significant |
| Pure Error | 69.5 | 4 | 17.38 | | | |
| Cor Total ^d | 4292.82 | 21 | | | | |

^a Degrees of freedom.

^b Test for comparing model variance with residual (error) variance.

^c Probability of seeing the observed F-value if the null hypothesis is true.

^d Totals of all information corrected for the mean.

To observe the effect of the factors on the response in more details, three-dimensional (3D) response surface and contour plots were constructed. These plots represent the relationship between the response and levels of two factors simultaneously, while the other factors are fixed at their central levels [21]. Fig. 2 depicts 3D response surface and contour plots of the effect of pH (*P*) and volume of extraction solvent (*E*) on the extraction recovery (response) in which the values of chelating agent (*L*) and sonication time (*t*) were fixed at 1100 mg L⁻¹ and 10 min, respectively. Both factors (*P* and *E*) demonstrated quadratic effects on the response; hence the maximum point is located inside the experimental region. The contour plot shows the precise location of the optimum point for these parameters. The response increased up to about pH of 3.8 followed by a decline with its further increase. The contour plot indicates that the maximum recovery is located at pH values 3–4 and volume of extraction solvent at 97–110. The simultaneous effect of pH (*P*)

and concentration of chelating agent (*L*) on the extraction recovery (ER) is shown in Fig. 3, while the sonication time and volume of extraction solvent were held at 10 min and 75 μL, respectively. The pH shows a quadratic effect on the response yielding the maximum between 4.2 and 5.4. Moreover, the chelating agent (*L*) influenced the response in different quadratic manners. At lower end of pH (3.8–4.6), the response increases with increasing *L* up to approximately 94% recovery. However, at upper end of pH (4.6–6.1), the recovery decreased with increasing *L*. This effect indicates that pH values lower than 4.6 and the chelating agent concentrations higher than 1200 mg L⁻¹ favor the complexation, and hence the extraction. Considering the above discussions to obtain the maximum recovery of the analytes, the optimum set points of the parameters was determined as 98 μL for volume of extraction solvent (CCl₄), 1476 mg L⁻¹ for concentration of the chelating agent, 3.8 for pH, and 9 min for the sonication time.

3.3. Evaluation of the method performance

Under the optimal experimental conditions, the linear dynamic ranges (LDRs), determination coefficients (R²), limits of detection (LODs) and relative standard deviations (RSDs) were determined and summarized in Table 5. The calibration curves were prepared in the range of 1–500 μg L⁻¹ for Ga and 1–1000 μg L⁻¹ for the other analytes with ten concentration levels and were characterized with high correlation coefficients (R²) in the range of 0.991–0.998. The limits of detection (LODs) based on $C_{LOD} = 3S_b/m$ (where C_{LOD} , S_b and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively) were obtained between 0.13 and 0.52 μg L⁻¹. The limit of quantifications (LOQs) was calculated based on the standard deviation of the blank to the slope of the calibration graph (S_b/m). It was equal to 10. The relative standard deviations (RSDs, $n=6$, $C=200$ μg L⁻¹) were 1.87%–5.65%.

3.4. Effect of coexisting ions

To evaluate the selectivity of the proposed method for determination of trace levels of Al, Bi, Cd, Co, Cu, Fe, Ga, In, Ni, Pb, Tl and Zn, the potential interference from coexisting ions on the recovery of the analytes was investigated. For this purpose, 10 mL of the mixed solutions (200 μg L⁻¹) of the analytes with various amounts of interfering ions were treated according to the procedure mentioned in Section 2.3 and the results were given in Table 6. The possible interferences were evaluated as a ± 10% error in the recovery of the analytes. It was indicated that the presence of the common cations and anions in real water samples have no significant effect on the recovery of the analytes.

3.5. Accuracy of the method

The accuracy and applicability of the proposed procedure was investigated by determination the heavy metal ions into different reference materials (CRM-TMDW-500 drinking water and SLRS-4 riverine water). As can be seen in Table 7, the results are in good agreement with the certified values.

3.6. Analysis of real samples

To demonstrate the efficiency of the USAEME-ICP-OES method, it was applied to analysis of various real water (spiked and non-spiked) samples including tap, mineral and river waters. The relative recovery (RR) was obtained by using the following

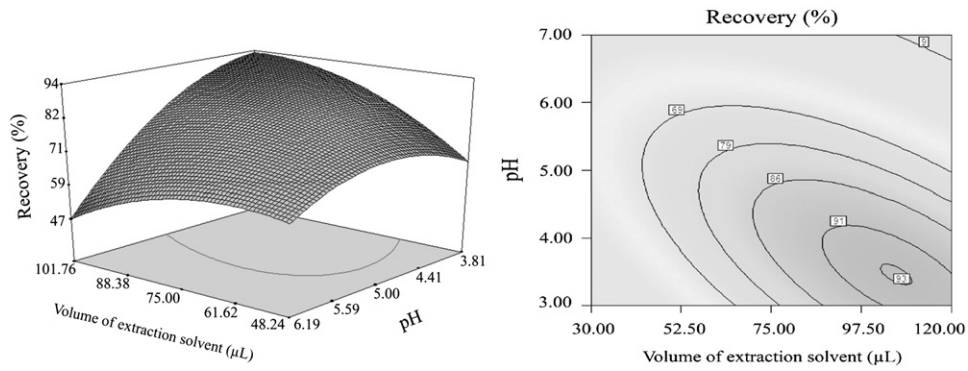


Fig. 2. 3D response surface and contour plots for the effect of volume of extraction solvent and pH at constant concentration of chelating agent of 1100 mg L⁻¹ and sonication time of 10 min on the average extraction recovery.

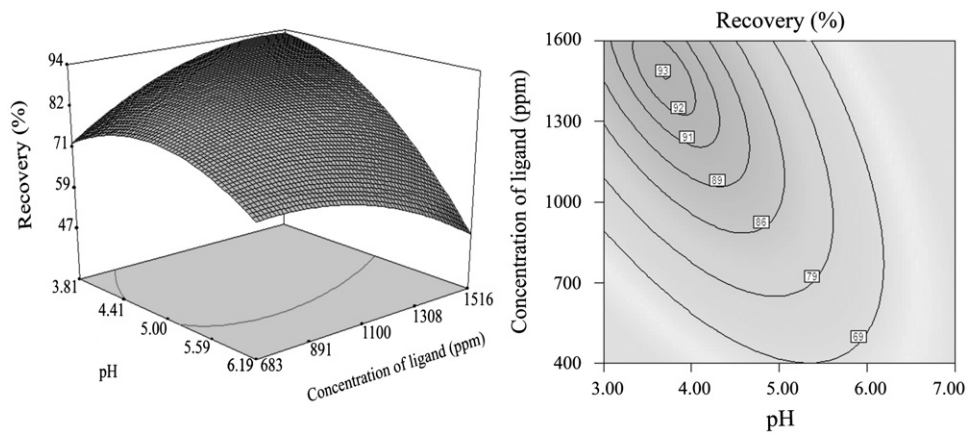


Fig. 3. 3D response surface and contour plots for concentration of chelating agent and pH at constant volume of extraction solvent of 75 μL and sonication time of 10 min on the average extraction recovery.

Table 5
Analytical figures of merit of the proposed method.

| Parameter | Al | Bi | Cd | Co | Cu | Fe | Ga | In | Ni | Pb | Tl | Zn |
|------------------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|
| LDR ^a | 1–1000 | 1–1000 | 1–1000 | 1–1000 | 1–1000 | 1–1000 | 1–500 | 1–1000 | 1–1000 | 1–1000 | 1–1000 | 1–1000 |
| R ^{2b} | 0.998 | 0.998 | 0.998 | 0.998 | 0.997 | 0.996 | 0.994 | 0.996 | 0.998 | 0.991 | 0.996 | 0.997 |
| EF ^c | 18 | 20 | 17 | 19 | 18 | 20 | 19 | 18 | 20 | 17 | 19 | 20 |
| LOD ^d | 0.13 | 0.48 | 0.19 | 0.28 | 0.29 | 0.27 | 0.27 | 0.38 | 0.44 | 0.47 | 0.52 | 0.17 |
| LOQ ^e | 0.43 | 1.60 | 0.63 | 0.93 | 0.96 | 0.90 | 0.90 | 1.25 | 1.45 | 1.55 | 1.72 | 0.56 |
| RSD ^f | 1.87 | 3.75 | 4.27 | 5.08 | 4.24 | 1.93 | 4.04 | 5.11 | 4.55 | 5.65 | 4.19 | 4.73 |

^a Linear dynamic range (μg L⁻¹).

^b Determination coefficient.

^c Enrichment factor.

^d Limit of detection (μg L⁻¹).

^e Limit of quantification (μg L⁻¹).

^f Relative standard deviation (C=200 μg L⁻¹, n=6).

Table 6
Effect of interfering ions on the recovery of heavy metal in water sample.

| Interference | Interference to analyte ratio (w/w) ^a | Recovery (%) | | | | | | | | | | | |
|-------------------------------|--|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | | Al | Bi | Cd | Co | Cu | Fe | Ga | In | Ni | Pb | Ti | Zn |
| Na ⁺ | 4000 | 98 | 104 | 98 | 101 | 99 | 100 | 99 | 97 | 95 | 102 | 104 | 98 |
| K ⁺ | 2000 | 101 | 104 | 100 | 97 | 106 | 102 | 104 | 95 | 96 | 96 | 97 | 104 |
| Mg ²⁺ | 2000 | 98 | 97 | 101 | 104 | 104 | 97 | 88 | 97 | 96 | 98 | 104 | 96 |
| Ca ²⁺ | 2000 | 100 | 101 | 104 | 98 | 96 | 100 | 100 | 95 | 98 | 105 | 95 | 97 |
| Mn ²⁺ | 50 | 95 | 96 | 105 | 102 | 105 | 96 | 93 | 100 | 101 | 105 | 100 | 97 |
| SO ₄ ²⁻ | 400 | 97 | 101 | 96 | 95 | 97 | 100 | 101 | 102 | 100 | 99 | 102 | 98 |
| CO ₃ ²⁻ | 400 | 96 | 104 | 96 | 95 | 100 | 98 | 99 | 99 | 96 | 101 | 104 | 103 |
| Cl ⁻ | 4000 | 98 | 102 | 99 | 100 | 99 | 97 | 99 | 98 | 104 | 100 | 96 | 96 |

^a Concentration of each analyte is 200 μg L⁻¹.

Table 7
Analysis of the two certified reference materials for the determination heavy metal ions with USAEME-ICP-OES method.

| CRM TMDW-500 drinking water | Al | Bi | Cd | Co | Cu | Fe |
|---|-------------------|----------------|-------------------|-------------------|-----------------|-----------------|
| Certified value ($\mu\text{g L}^{-1}$) | 120.0 \pm 0.6 | 10.0 \pm 0.1 | 10.00 \pm 0.05 | 25.0 \pm 0.1 | 20.0 \pm 0.1 | 100.0 \pm 0.5 |
| Amount found ($\mu\text{g L}^{-1}$) ^a | 121.1 \pm 0.1 | 9.5 \pm 0.2 | 9.64 \pm 0.02 | 25.4 \pm 0.4 | 19.7 \pm 0.3 | 102.8 \pm 0.6 |
| Recovery (%) | 100.92 | 95.00 | 96.40 | 101.60 | 98.50 | 102.78 |
| CRM TMDW-500 Drinking Water | Ga | In | Ni | Pb | Tl | Zn |
| Certified value ($\mu\text{g L}^{-1}$) | n.r. ^b | n.r. | 60.0 \pm 0.3 | 40.0 \pm 0.2 | n.r. | 70.0 \pm 0.4 |
| Amount found ($\mu\text{g L}^{-1}$) | n.d. | n.d. | 57.3 \pm 0.2 | 41.3 \pm 0.5 | n.d. | 68.7 \pm 0.6 |
| Recovery (%) | – | – | 95.53 | 103.37 | – | 98.21 |
| NRCC-SLRS 4 riverine water ($\mu\text{g L}^{-1}$) | Al | Bi | Cd | Co | Cu | Fe |
| Certified value ($\mu\text{g L}^{-1}$) | 54 \pm 4 | n.r. | 0.012 \pm 0.002 | 0.033 \pm 0.006 | 1.81 \pm 0.08 | 103 \pm 5 |
| Added ($\mu\text{g L}^{-1}$) | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Amount found ($\mu\text{g L}^{-1}$) | 59 \pm 2 | 4.9 \pm 0.2 | 4.9 \pm 0.4 | 4.89 \pm 0.02 | 6.95 \pm 0.04 | 108 \pm 4 |
| Recovery (%) | 99.80 | 97.40 | 98.76 | 97.15 | 102.05 | 100 \pm 3 |
| NRCC-SLRS 4 riverine water ($\mu\text{g L}^{-1}$) | Ga | In | Ni | Pb | Tl | Zn |
| Certified value ($\mu\text{g L}^{-1}$) | n.r. | n.r. | 0.67 \pm 0.08 | 0.086 \pm 0.007 | n.r. | 0.93 \pm 0.10 |
| Added ($\mu\text{g L}^{-1}$) | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Amount found ($\mu\text{g L}^{-1}$) | 4.9 \pm 0.3 | 4.8 \pm 0.5 | 5.56 \pm 0.05 | 5.01 \pm 0.02 | 4.9 \pm 0.1 | 6.1 \pm 0.3 |
| Recovery (%) | 97.2 | 95.2 | 98.06 | 98.48 | 97.8 | 103.2 |

^a Average \pm standard deviation ($n=3$).

^b Not reported.

Table 8
Trace determination of Al, Bi, Cd, Co, Cu, Fe, Ga, In, Ni, Pb, Tl and Zn in different water samples.

| Element | Tap water ^a | | | Mineral water ^d | | | River water ^e | | | | | |
|---------|--------------------------------|---|------------------------|--------------------------------|--------------------------------|-----------|--------------------------------|---------------------------------|-----------------|----|-----------------|-------|
| | Added ($\mu\text{g L}^{-1}$) | Found ^c ($\mu\text{g L}^{-1}$) | R. R. ^f (%) | Added ($\mu\text{g L}^{-1}$) | Found ($\mu\text{g L}^{-1}$) | R. R. (%) | Added ($\mu\text{g L}^{-1}$) | Found. ($\mu\text{g L}^{-1}$) | R. R. (%) | | | |
| Al | 27.4 \pm 1.5 | 20 | 48.2 \pm 1.14 | 103.7 | 17.6 \pm 0.50 | 20 | 38.7 \pm 0.79 | 105.5 | 7.8 \pm 0.54 | 20 | 27.0 \pm 0.88 | 95.8 |
| Bi | n.d. ^b | 20 | 19.5 \pm 0.81 | 97.3 | n.d. | 20 | 19.8 \pm 0.61 | 99.0 | n.d. | 20 | 19.5 \pm 1.30 | 97.3 |
| Cd | n.d. | 20 | 19.9 \pm 0.18 | 99.4 | n.d. | 20 | 20.0 \pm 0.06 | 100.1 | n.d. | 20 | 19.7 \pm 0.30 | 98.5 |
| Co | n.d. | 20 | 19.9 \pm 0.12 | 99.4 | n.d. | 20 | 19.3 \pm 1.16 | 96.3 | n.d. | 20 | 19.3 \pm 0.58 | 96.3 |
| Cu | 13.2 \pm 0.34 | 20 | 32.5 \pm 0.63 | 96.3 | 6.2 \pm 0.41 | 20 | 26.9 \pm 0.33 | 103.6 | 26.9 \pm 1.2 | 20 | 46.3 \pm 0.87 | 97.0 |
| Fe | 14.7 \pm 0.65 | 20 | 35.0 \pm 0.67 | 101.5 | 10.0 \pm 0.31 | 20 | 29.7 \pm 1.26 | 98.3 | 9.8 \pm 0.65 | 20 | 28.9 \pm 0.75 | 95.8 |
| Ga | n.d. | 20 | 19.7 \pm 0.05 | 98.4 | n.d. | 20 | 18.1 \pm 3.42 | 90.3 | n.d. | 20 | 19.8 \pm 0.05 | 99.0 |
| In | n.d. | 20 | 19.4 \pm 0.74 | 97.0 | n.d. | 20 | 19.3 \pm 0.94 | 96.7 | n.d. | 20 | 19.7 \pm 0.34 | 98.3 |
| Ni | n.d. | 20 | 19.8 \pm 0.16 | 99.2 | n.d. | 20 | 19.5 \pm 0.49 | 97.4 | n.d. | 20 | 19.6 \pm 0.80 | 97.9 |
| Pb | n.d. | 20 | 20.0 \pm 1.16 | 99.9 | n.d. | 20 | 19.6 \pm 0.18 | 98.0 | n.d. | 20 | 20.3 \pm 0.73 | 101.3 |
| Tl | n.d. | 20 | 19.1 \pm 1.01 | 95.4 | n.d. | 20 | 19.2 \pm 0.99 | 95.8 | n.d. | 20 | 19.3 \pm 1.65 | 96.3 |
| Zn | 60.1 \pm 1.6 | 20 | 79.9 \pm 0.58 | 99.1 | 9.2 \pm 0.65 | 20 | 29.6 \pm 0.64 | 101.9 | 44.8 \pm 0.94 | 20 | 64.5 \pm 0.63 | 98.2 |

^a The tap water was taken from university of Tehran (Tehran, capital of Iran).

^b Not detected.

^c Mean \pm SD % ($n=3$).

^d Mineral water was prepared from Nestle company (Damavand city, Tehran province).

^e The sample was collected from Langroud river (Gilan province, north of Iran).

^f Relative recovery.

Table 9
Comparison of the proposed method with CPE and SPE for determination of elements in water samples.

| Element | Method | LDR ^b | LOD ^c | RSD | Detection | Ref. |
|--|--------|------------------|--|----------|-----------|-----------|
| Al, Bi, Cd, Co, Cu, Fe, Ga ³ , In, Ni, Pb, Tl, Zn | USAEME | 1–1000 | 0.13,0.48,0.19,0.28,0.29,0.27, 0.27,0.38,0.44,0.47,0.52,0.17 | 1.87–5.6 | ICP-OES | This work |
| Cd, Co, Ni, Pb, Zn | SPE | 1–400 | 0.3,0.7,0.6,0.8,0.2 | 1.7–3.2 | ICP-OES | [22] |
| Al, Cu, Fe, Zn | USAEME | 1–1000 | 0.83,0.72,0.64,0.91 | 2.6–5.3 | ICP-OES | [23] |
| Cu, Cd, Ni, Zn | CPE | 50–2500 | 1.2,1.6,1.1 | 1.3–2.6 | ICP-OES | [24] |
| Cu, Mn, Fe, Cd, Co, Ni, Pb, Zn | SPE | 25–5000 | 0.16–0.60 | 1.0–17.0 | FAAS | [25] |

^a LDR for Ga was 1–500 ($\mu\text{g L}^{-1}$).

^b Linear dynamic range ($\mu\text{g L}^{-1}$).

^c Limit of detection ($\mu\text{g L}^{-1}$).

equation (Eq. (7)):

$$RR = \frac{C_{\text{found}} - C_{\text{real}}}{C_{\text{added}}} \quad (7)$$

where C_{found} , C_{real} , and C_{added} are the concentration of analyte in the final solution after addition of a known amount of a standard

into the real sample, the concentration of analyte in the real sample and the concentration of a known amount of the standard which was spiked into the real sample, respectively. The obtained results (Table 8) indicate that the relative recoveries for the spiked samples are acceptable (90.3%–105.5%) and the sample matrices had a little effect on the extraction efficiency.

3.7. Comparison with other analytical methods

Analytical specifications of the proposed method with other previously reported methods for simultaneous extraction and determination of similar metal ions were compared and summarized in Table 9. The LOD of this method is lower than the other methods. The LDR is better than SPE-ICP-OES, SPE-FAAS and CPE-ICP-OES methods. The RSD is comparable with that of the other methods.

4. Conclusion

Application of ultrasound offers advantages like improved efficiency, reduced extraction time, low solvent consumption. Ultrasound-assisted microextraction (USAEME) is an inexpensive, simple and environmental friendly method that increases the contact surface area between the extraction solvent and the analyte solution at room temperature. In addition, there is no chemical involvement which could prevent possible chemical degradation of targeted compounds. The extraction step of the method was optimized and modeled with the minimum number of the experiments by the aid of response surface methodology. The combination of optimized USAEME with ICP-OES was an effective technique for simultaneous multielement trace analysis of heavy metals in water samples.

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