

Optimization and determination of Cd (II) in different environmental water samples with dispersive liquid–liquid microextraction preconcentration combined with inductively coupled plasma optical emission spectrometry

Maryam Salahinejad · Fereydoon Aflaki

Received: 27 October 2009 / Accepted: 9 July 2010 / Published online: 23 July 2010
© Springer Science+Business Media B.V. 2010

Abstract Dispersive liquid–liquid microextraction followed by inductively coupled plasma-optical emission spectrometry has been investigated for determination of Cd(II) ions in water samples. Ammonium pyrrolidine dithiocarbamate was used as chelating agent. Several factors influencing the microextraction efficiency of Cd (II) ions such as extracting and dispersing solvent type and their volumes, pH, sample volume, and salting effect were optimized. The optimization was performed both via one variable at a time, and central composite design methods and the optimum conditions were selected. Both optimization methods showed nearly the same results: sample size 5 mL; dispersive solvent ethanol; dispersive solvent volume 2 mL; extracting solvent chloroform; extracting solvent volume 200 μL ; pH and salt amount do not affect significantly the microextraction efficiency. The limits of detection and quantification were 0.8 and 2.5 ng L^{-1} , respectively. The relative standard deviation for five replicate measurements of 0.50 mg L^{-1} of Cd

(II) was 4.4%. The recoveries for the spiked real samples from tap, mineral, river, dam, and sea waters samples ranged from 92.2% to 104.5%.

Keywords Dispersive liquid–liquid microextraction · One-variable-at-a-time · Central composite design · Cd (II) · Environmental water samples

Introduction

Cadmium (Cd) is a heavy metal of considerable environmental and occupational concern. Sources of exposure to cadmium include diet, drinking water, cigarette smoking, and occupational exposure (Agency of Toxic Substances and Disease Registry 1999). Cadmium is a toxic metal that can cause several health effects (Jarup et al. 1998), mainly kidney and bone damage, even in non-occupationally exposed populations (Jarup 2003; Jarup and Alfven 2004). Cadmium has been implicated in the development of various types of cancer (Waalkes 2003). It has been classified as carcinogenic by the International Agency for Research on Cancer, with exposure being primarily associated with lung cancer (International Agency for Research on Cancer 1997).

Despite the sensitivity and selectivity of analytical techniques such as atomic absorption spectrometry (Wuilloud et al. 2008) and inductively

M. Salahinejad (✉) · F. Aflaki
Environmental Laboratory, Nuclear Science Research
School, Nuclear Science and Technology Research
Institute, Atomic Energy Organization of Iran
(AEOI), P.O. Box 11365-3486, Tehran, Iran
e-mail: salahinejad@gmail.com

coupled plasma (Batterham et al. 1997; Li et al. 1996), there is a crucial need for the pre-concentration of trace elements before their analysis due to their low concentrations and matrix effects in environmental samples especially water samples. The most frequently employed methods for pre-concentration are liquid–liquid extraction (Anthemidis et al. 2003), co-precipitation (Atsumi et al. 2005), solid phase extraction (Yamini et al. 2003; Melek et al. 2006), and cloud point extraction (Chen et al. 2005).

Dispersive liquid–liquid microextraction (DLLME) is a new microextraction technique which was reported and used for the first time in 2006, by Assadi et al. (Rezaee et al. 2006). In this method, an appropriate mixture of extraction and dispersive solvents is injected rapidly into an aqueous sample with a syringe, resulting in the formation of a cloudy solution. Phase separation is performed by centrifugation and the enriched analyte in the sediment phase was determined. It is simple, rapid, and efficient, with high enrichment factors and recovery (Ojeda and Rojas 2009). Since its introduction, this method has been applied for the determination of trace organic pollutants and metal ions in environmental water samples (Fatahi et al. 2007; Liang and Sang 2008; Berijani et al. 2006; Jiang et al. 2008).

In the present work, DLLME followed by inductively coupled plasma-optical emission spectrometry (ICP-OES) has been investigated for determination of Cd (II) in water samples. Several factors influencing the microextraction efficiency such as extraction and dispersive solvent type and their volumes, pH, sample volume, and salting effect were optimized using two methods: one variable at a time and simultaneous optimization method. Central composite design (CCD) and response surface methodology were used as experimental strategies for modeling and optimization of the method. The goal of the proposed work was to describe in details the effects of various parameters by modeling enrichment factor, recovery, and sediment phase volume as three antagonist responses. The influence of each parameter and their interactions could be well identified for different responses screened. The purpose of experimental designs is to deliver as much informa-

tion as possible with a minimum of experimental or financial effort (Gemperline 2006).

Experimental

Instrumentation

A Perkin Elmer dual-view ICP-AES instrument, Model Optima 2100DV (Norwalk, CT, USA) and a Rotofix 32 centrifuge from Zentrifugen Co (Germany) were used. The pH values were measured with a Mettler Toldo pH/Ion-Analyzer, Model MA235 (Herisau, Switzerland), supplied with a glass-combined electrode. Table 1 shows the instrumental and operating conditions for ICP-AES measurements.

Reagents and solutions

The stock solution of cadmium (1,000 mg L⁻¹ for ICP-AES standard) was purchased from Merck (Darmstadt, Germany). Working solutions were prepared by diluting the stock standard as necessary. Deionized water obtained by a Milli-Q system (Millipore, Milford, USA) was used for standard dilutions and other necessary preparations. Ammonium pyrrolidine dithiocarbamate (APDC, 0.1M) solution was prepared, on a hot-plate stirrer at approximately 50°C, by dissolving the appropriate amount of APDC (analytical grade, Merck) in ethanol (extra pure, Merck). All other chemicals such as carbon tetrachloride (extra pure), chloroform (extra pure), and dichloromethane (extra pure) as extracting solvents, methanol (for liquid chromatography), acetone (extra pure), and acetonitrile (HPLC grade)

Table 1 Operation parameters for ICP-OES

Parameters	
RF Power (Watt)	1,300
Nebulizer gas flow rate (L min ⁻¹)	0.8
Auxiliary gas flow rate (L min ⁻¹)	0.2
Plasma gas flow rate (L min ⁻¹)	15
Sample flow rate (mL min ⁻¹)	1
Wavelength (nm) for Cd(II)	228.802
Plasma viewing	Axial
Processing mode	Area
Delay time (s)	20

as dispersive solvents, HNO₃ (65%, supra pure), CH₃COONa (supra pure), NaNO₃ (analytical grade), and NH₃ (25%, supra pure) were supplied from Merck.

General procedure

In a typical experiment, to 5 mL of 0.5 mg L⁻¹ Cd (II) solution in a 12-mL test tube with conical bottom, 2 mL of ethanol (dispersive solvent) containing 0.1 M APDC (chelating agent), and 200 μL of chloroform (extraction solvent) simultaneously was injected into the sample solution by using a 5-mL syringe. A cloudy solution was formed in the test tube. Cd (II) reacts with APDC and extracted into the fine droplets of chloroform. The mixture centrifuged at 3,000 rpm for 5 min until the fine droplets of chloroform were sedimented at the bottom of the conical sample tube. The sedimented phase was quantitatively transferred (by a Hamilton 200-μL syringe) to another test tube and allowed to evaporate of chloroform at room temperature. The residue was dissolved into 0.5 mL of 0.1 M nitric acid and the Cd (II) concentration was determined by ICP-AES. The effect of different parameters affecting the enrichment factor such as kind of dispersive and extraction solvents and their volumes, sample size, pH, and salt effect was studied. Equation 1 was used for calculation of the enrichment factor.

$$EF = C_{sed}/C_0 \tag{1}$$

where EF, C_{sed}, and C₀ are the enrichment factor, concentration of the analyte in the sedimented phase, and initial concentration of the analyte in the aqueous sample, respectively.

The stock solution of cadmium (50 mg L⁻¹) was kept at room temperature and working solutions

of cadmium (0.2–10 mg L⁻¹) in 0.1 M nitric acid were prepared daily. All experiments were performed in duplicate, and the mean results were employed for plotting the necessary curves or tables which needed for optimization procedure.

Statistical software

Essential Regression and Experimental Design for Chemists and Engineers, EREGRESS, as a Microsoft Excel Add-In software (Stephan et al. 1998) was used to design the experiments and to model and analyze the results.

Optimization process of experimental design

The objective of the experimental design was to determine the main parameters influencing the enrichment factor, as well as recovery and sedimented phase of the DLLME method. CCD was used to optimize the preconcentration of Cd (II) by dispersive liquid–liquid microextraction. Five independent variables, including volume of extracting solvent (F₁), volume of dispersive solvent (F₂), pH (F₃), salting effect (F₄), and sample volume (F₅), were studied at five levels with four repeats at center point using CCD. The APDC concentration was selected 0.1 M in all experiments. The assignment of variables, their levels, and symbols of CCD are shown in Table 2. Table 3 shows the coded values of designed experiments, based on CCD methodology achieved using EREGRESS software, and the three responses, recovery percentage (R), enrichment factor (EF), and volume (μL) of sedimented phase (Vs), for central composite design.

Central composite design combines a two-level factorial design with additional points (star points) and at least one point at the center of the

Table 2 Assignment of factors, their levels and symbols of CCD

Variable	Symbol	Variable levels			Star points (α = 2)	
		-1	0	1	-α	+α
Volume of extracting solvent (μL)	F ₁	200	300	400	100	500
Volume of dispersive solvent (mL)	F ₂	1	2	3	0	4
pH	F ₃	4	6	8	2	10
Salt effect (%)	F ₄	1	3	5	0	10
Sample volume (mL)	F ₅	10	15	20	5	25

Table 3 Design matrix and the responses for CCD

Design points	Factor levels					Response		
	F ₁	F ₂	F ₃	F ₄	F ₅	EF	R (%)	V _{Sed} (μL)
1	0	2	0	0	0	112	63.73	85.36
2	1	-1	-1	-1	-1	250	41.00	16.40
3	1	1	-1	-1	1	184	57.38	62.36
4	-1	-1	-1	-1	1	38	13.38	70.39
5 (CP)	0	0	0	0	0	136	41.70	45.99
6	1	1	-1	1	-1	258	71.35	27.66
7	-1	-1	1	-1	-1	78	35.25	45.19
8 (CP)	0	0	0	0	0	128	38.30	44.88
9	-1	1	-1	1	1	34	22.70	133.53
10	0	0	0	0	-2	198	72.70	18.36
11	0	0	-2	0	0	136	51.03	56.29
12	0	0	0	2	0	152	38.03	37.53
13	0	0	0	0	2	50	19.58	97.90
14 (CP)	0	0	0	0	0	128	42.23	49.49
15	-1	-1	-1	1	-1	74	33.22	44.89
16	1	-1	1	1	-1	280	29.30	10.46
17	1	1	1	-1	-1	272	67.65	24.87
18	2	0	0	0	0	308	40.57	19.76
19	1	-1	1	-1	1	216	21.48	19.88
20	-1	1	1	-1	1	38	19.83	104.34
21	-1	1	1	1	-1	62	31.55	50.89
22	-1	1	-1	-1	-1	96	44.30	46.15
23 (CP)	0	0	0	0	0	132	41.30	46.93
24	0	0	2	0	0	134	42.27	47.31
25	-2	0	0	0	0	2	1.00	75.00
26	1	-1	-1	1	1	220	23.40	21.27
27	0	0	0	-2	0	72	31.37	65.35
28	1	1	1	1	1	202	55.50	54.95
29	0	-2	0	0	0	120	12.53	15.67
30	-1	-1	1	1	1	50	14.45	57.80

CP center point

experimental region to obtain properties such as rotatability or orthogonality, in order to fit quadratic polynomials. A factorial design ($2k$) is augmented with ($2k$) star points, where k is the number of variables to be optimized, and with a central point, which can be run n times (Myers and Montgomery 2002). Center points are usually repeated to get a good estimate of experimental error (pure error). Star points were located at $\pm\alpha$ from the centre of the experimental domain, which is $\alpha = \sqrt[4]{2^k}$, to make the experimental design rotatable and orthogonal (Myers and Montgomery 2002; Hinkelmann and Kempthorne 2007). The five-level factorial design of CCD allows an estimate of the response curvature and fitting of a quadratic model to the data. For an experimental design with five factors, this model that is shown in Eq. 2, consisted of three main

effects, three two-factor interaction effects, and three curvature effects, where b_0 is the intercept and the b terms represent those parameters obtained through multiple linear regression using EREGRESS.

$$\begin{aligned}
 \text{Response} = & b_0 + b_1F_1 + b_2F_2 + b_3F_3 + b_4F_4 \\
 & + b_5F_5 + b_6F_1 \times F_1 + b_7F_2 \times F_2 \\
 & + b_8F_3 \times F_3 + b_9F_4 \times F_4 + b_{10}F_5 \\
 & \times F_5 + b_{11}F_1 \times F_2 + b_{12}F_1 \times F_3 \\
 & + b_{13}F_1 \times F_4 + b_{14}F_1 \times F_5 + b_{15}F_2 \\
 & \times F_3 + b_{16}F_2 \times F_4 + b_{17}F_2 \times F_5 \\
 & + b_{19}F_3 \times F_4 + b_{19}F_3 \times F_5 \\
 & + b_{20}F_4 \times F_5
 \end{aligned} \tag{2}$$

The statistical significance of the full quadratic models prediction was evaluated by analysis of variance (ANOVA) and the least-squares technique. ANOVA consists in determining which of the factors significantly affect the response, using a Fisher’s statistical test (*F* test). The significance and magnitude of the estimated coefficients of each variable and all their possible linear and quadratic interactions are determined. The coefficients for each variable represent the improvement in the response expected as the variable setting is changed from low to high. Effects with less than 95% significance, that is effects for which $P > 0.05$, were discarded and pooled into the error term, and a new analysis of variance was performed for the reduced model. Response-surface plots were obtained by use of a statistical process that described the design and modeled the CCD data. Response-surface methods graphically illustrate relationships between conditions and responses and are a means of obtaining an exact optimum (Lundstedt et al. 1998; Araujo and Breerton 1996).

Result and discussion

One-variable-at-a-time method

Selection of dispersive and extraction solvents

The most important point for the selection of the dispersive solvent is its miscibility with both organic (extracting solvent) and aqueous (sample solution) phases. For this purpose, different solvents such as acetone, acetonitrile, methanol, and ethanol were examined. The extraction solvent should demonstrate a higher density than water. Such solvents are mainly chlorinated and among them, chloroform, carbon tetrachloride, and dichloromethane were investigated for the cadmium preconcentration.

In Fig. 1, the EF is shown for all combinations of dispersive and extracting solvents. For dichloromethane as extraction solvent, two-phase system was just observed by acetone as dispersive solvent. No sedimented phase was obtained in the combination of dichloromethane as extraction solvent and methanol, ethanol, and acetonitrile

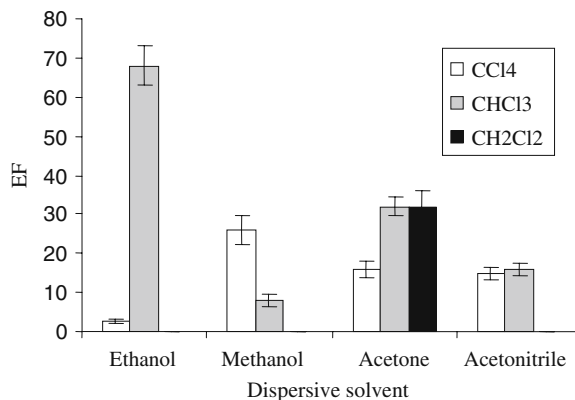


Fig. 1 Selection of extracting and dispersive solvent, Conditions: sample, 5 mL of Cd^{2+} , $0.5 \mu g mL^{-1}$; volume of dispersive solvent, 2 mL; volume of extracting solvent, 200 μL ; pH = 4 and APDC 0.1 M. The bars show the maximum and minimum levels of determinations

as dispersive solvent; hence, these conditions are useless. Considering the sedimented phase volume, it was found that in the combination of chloroform and carbon tetrachloride with methanol, the sedimented phase volume was about 370 μL , and in the combination of chloroform and carbon tetrachloride acetonitrile, the sedimented phase volume was about 480 μL ; therefore, these combinations had low EF. Chloroform with acetone showed attainable recovery, but it showed low EF.

Among these different combination of extraction and dispersive solvents, chloroform–ethanol showed the highest EF and reasonable recovery; therefore, chloroform and ethanol were selected as the extracting and dispersive solvents for DLLME of Cd (II).

Effect of dispersive solvent volume

Ethanol as a dispersive solvent in different volumes, 1–4 mL in 0.5-mL intervals, with 200 μL chloroform as extracting solvent, was used for extraction of Cd (II) by use of DLLME. As shown in Fig. 2, the enrichment factor increased by increasing the ethanol volumes. In the case of 2 mL ethanol, the highest recovery and a reasonable EF and sedimented phase volume are attainable, but in the higher volume of ethanol, the recovery decreased; therefore, we chose 2 mL ethanol as

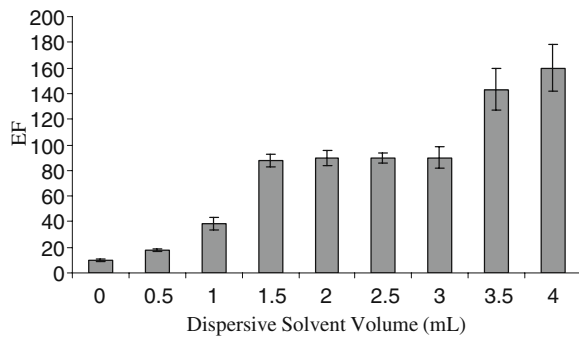


Fig. 2 Effect of dispersive solvent volume, others conditions are the same as Fig. 1

the optimum volume of disperser solvent for Cd (II) DLLME procedure.

Effect of extraction solvent volume

To examine the effect of the extracting solvent volume, 2 mL ethanol solutions with different chloroform volumes, in the range of 50–500 μL , were subjected to the same DLLME procedure. Figure 3 depicts the variation of the enrichment factor versus the volume of the extracting solvent. There was no sedimented organic phase in the case of 50 μL , and the system became useless. Enrichment factors decrease with the increase of the chloroform volume, owing to the sedimented phase volume increase. By using 100- μL chloroform, EF 75 and recovery 35% were obtained for cadmium ions. The volume of sedimented phase was very low in this condition. In the case of

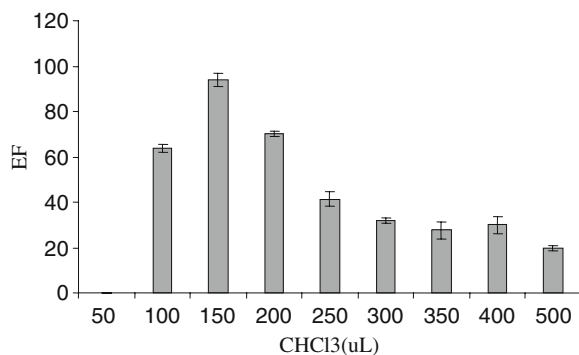


Fig. 3 Effect of extracting solvent volume, others conditions are the same as Fig. 1

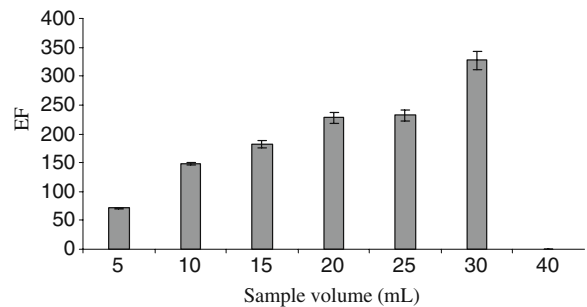


Fig. 4 Effect of sample volume, others conditions are the same as Fig. 1

200 μL chloroform, high recovery (more than 90%) and reasonable EF was achieved; therefore, 200- μL chloroform was selected as the optimum value for further studies.

Effect of sample size

Different volumes of sample solution (5–50 mL) were used to study the effect of sample size with a constant volume of extracting solvent (200 μL) and dispersive solvent (2 mL). The results (Fig. 4) show that with a large sample size (40–50 mL), no sedimented phase was obtained. By increasing the sample size from 5 to 30 mL, the volume of sedimented phase and recovery decreased whereas EF increased. With 2 mL ethanol and 200 μL chloroform, a higher recovery and reasonable EF and sedimented phase volume for sample size of 5 mL was achieved; thus, sample size of 5 mL was chosen in the further studies.

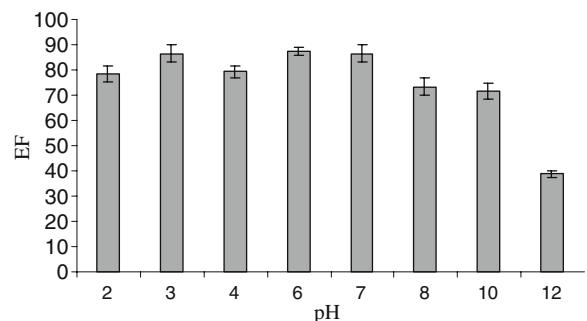


Fig. 5 Effect of pH, others conditions are the same as Fig. 1

Table 4 Some characterizations of constructed models

Response	R^2	$R^2_{\text{adjustment}}$	$R^2_{\text{prediction}}$	Regression equation
Enrichment factor (EF)	0.928	0.913	0.883	$EF = b_0 + b_1F_2 + b_2F_1 + b_3F_5 + b_4F_2 \times F_5 + b_5F_1 \times F_5$
Recovery (R)	0.928	0.913	0.893	$R = b_0 + b_1F_2 + b_2F_1 + b_3F_5 + b_4F_2 \times F_1 + b_5F_1 \times F_1$
Sedimented phase volume (Vs)	0.952	0.946	0.925	$Vs = b_0 + b_1F_1 + b_2F_5 + b_3F_1 \times F_1$

Effect of pH

pH can play a unique role on metal–chelate formation and the production of extractable species from ionic analytes prior to extraction by DLLME. The effect of pH on the complex formation and extraction of cadmium ions from water samples was studied in the range of 2–12 by using HNO₃, CH₃COONa, and NH₃. The results illustrated in Fig. 5 reveal that the production of metal–chelate and its extraction is pH-independent between pH 2 and 10, and pH does not influence the sedimented phase volume significantly. In this range, the highest FE and recovery are obtained. Thus, pH 4 was selected for following studies.

Salting effect

Salt addition is frequently used to adjust the ionic strength, improve the extraction efficiency and reduce the detection limit. The effect of the ionic strength on the cadmium efficiency factor by DLLME was examined across the concentration range of 0–10% (w/v) NaNO₃. The data from these experiments presented that the salt addition did not significantly influence the enrichment factor for Cd(II). As a consequence, all the ex-

traction experiments were carried out without salt addition.

Central composite design

The volumes of extracting solvent (F₁) and dispersive solvent (F₂), pH (F₃), salt (NaNO₃) amount (F₄), and sample volume (F₅) were chosen to be optimized simultaneously using the data acquired from 30 sets of experiments performed according to the CCD method. Three antagonist criteria namely enrichment factor, recovery percentage, and sedimented phase volume were investigated as responses in order to optimize five mentioned variables. The levels of coded and actual experimental variables tested are presented in Table 2. The levels of coded experimental variables, based on CCD methodology achieved using EREGRESS software and the respective response values of central composite design, are presented in Table 3. The five-level factorial design allows for the fitting of a quadratic model to the data. With a full quadratic model including all terms as in Eq. 2, finding the significant factors and build a model to optimize the DLLME procedure was possible. The insignificant terms ($P > 0.05$) were eliminated from the model through

Table 5 Coded and uncoded constants and coefficients for the constructed quadratic models (equations represented in Table 3)

	Enrichment factor		Recovery		Sedimented phase volume	
	Coded values	Uncoded values	Coded values	Uncoded values	Coded values	Uncoded values
b_0	49.90	22.45	41.34	16.81	131.33	46.33
b_1	14.91	−13.82	10.88	−10.61	84.33	0.29
b_2	−17.74	0.01	9.65	0.26	−28.50	−5.7
b_3	17.38	3.39	−9.66	−1.93	9.17	0.00
b_4	9.58	1.92	7.16	0.07		
b_5	−6.24	−0.01	−5.09	0.00		

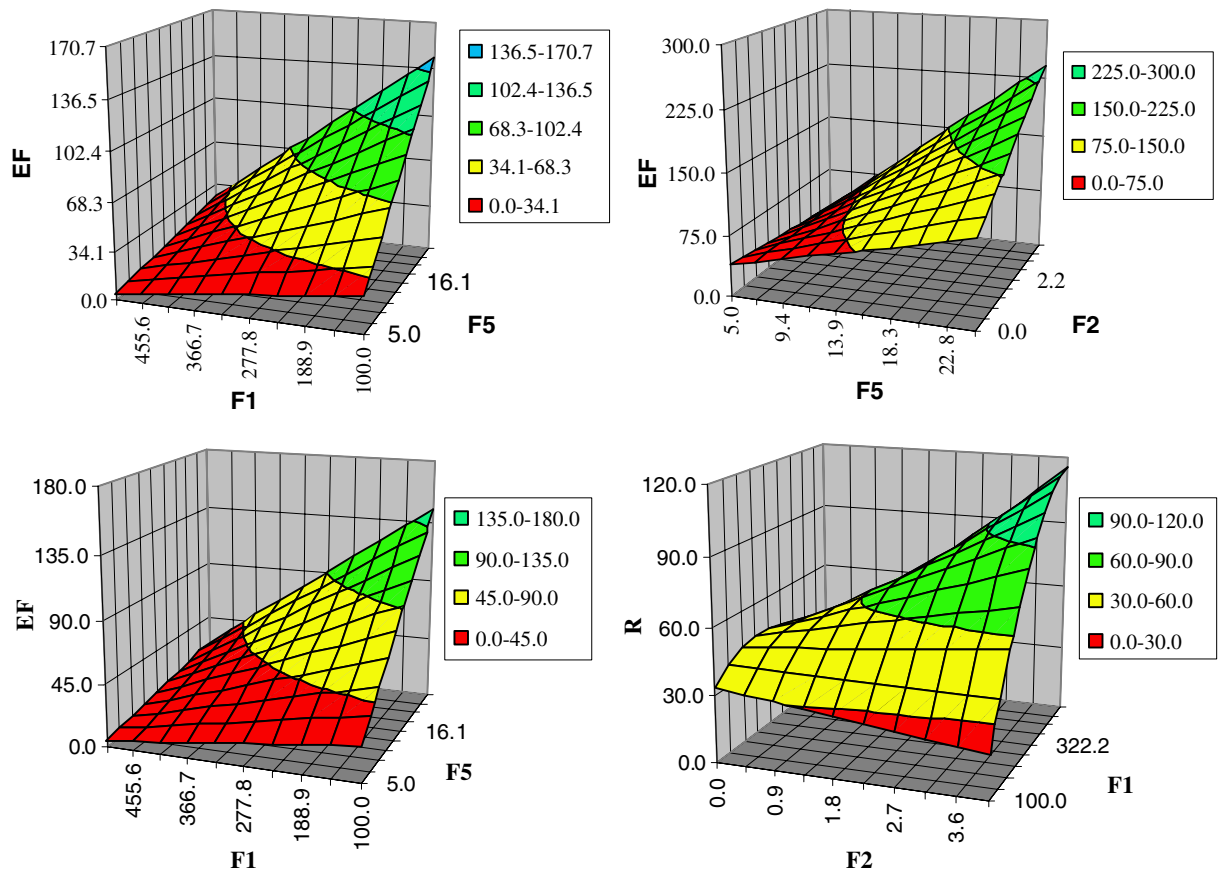


Fig. 6 Response surface modeling of enrichment factor (EF) and recovery (R): volume of extracting solvent (F_1), dispersive solvent (F_2), and sample solution (F_5)

the “backward elimination” process. The main characteristics of the reduced models are given in Tables 4 and 5. In the present study, the adjusted R^2 were well within the acceptable limits of $R^2 \geq 0.9$, and there is little difference between R^2 s which revealed that the experimental data show a good fit with the second-order polynomial equations (Table 4). The plots of predicted responses versus calculated ones showed that the residual

values were significantly low; for example, the regression equation for predictive recovery versus calculated ones were obtained as: $Y = 0.9279X + 2.6865$ with $R^2 = 0.9279$.

As can be seen from Tables 4 and 5, pH (F_3) and salt amount (F_4) had no significant effect on EF , recovery, and sedimented phase volume and did not enter in constructed models. Volume of ethanol as extracting solvent (F_1), volume of

Table 6 Optimum conditions obtained by RMS for enrichment factor, recovery, and sedimented phase volume

Variable	Optimum values			
	EF	R	Vs	Selected optimum value
Extraction solvent volume, F_1 (mL)	< 200	200–300	200–300	200
Disperser solvent volume, F_2 (μ L)	1.5–2.5	2–3	No effect	2
Sample volume, F_5 (mL)	5	15–20	< 15	5

chloroform as dispersive solvent (F_2), and sample volume (F_3) affect significantly the EF modeling by linear variables. The main interaction variables for EF modeling were obtained as $F_2 \times F_5$ and $F_1 \times F_5$. Extracting solvent volume (F_1) affects significantly the recovery modeling by linear, interaction (as $F_2 \times F_1$) and quadratic variables. The next significant factors on recovery modeling were volume of dispersive solvent (F_2), with both linear and interaction (as $F_2 \times F_1$) variables and sample volume with only linear variable. When using sedimented phase volume as model response, extracting solvent volume (F_1) affects the model by both linear and quadratic variables, and sample volume (F_5) affects the model by only linear variables.

Response surface modeling and selection of optimum conditions

The three-dimensional response surfaces plots relating responses with independent variables generated by EREGRESS software. The plots shown in Fig. 6 represent response surface modeling (RMS) of enrichment factor and recovery. These figure show the interaction between two interacting factors when other factors have been kept constant using the constructed models. The selection of optimum conditions was possible from the RMS plots. The criteria for optimum value selection were set as follows: recovery near to 100, sedimented phase volume more than 50 μL , and enrichment factor as high as possible. The conditions that meet these requirements are shown in Table 6.

Analytical performance

Quality variables including the limit of detection (LOD) and precision (as relative standard deviation (RSD))

)) were investigated to evaluate the analytical performance of proposed method. According to IUPAC identification, LOD (3δ) of proposed method was 0.8 ng mL^{-1} with an enrichment factor of 75 for Cd (II). The RSD was 4.4% ($C = 0.5 \text{ } \mu\text{g mL}^{-1}$, $n = 5$) for Cd. The regression equation for calibration curves for Cd (II) after DLLME was $y = 1111 + 146300x$ with correlation coefficient (R^2) of 0.99997 where y is the signal intensity and x is the concentration of analyte in the extraction solvent.

Interferences effects

The effects of interferences in environmental water samples on the recovery of cadmium were studied. The effect of alkali and alkali earth metals (Li^+ , K^+ , Na^+ , Sr^{2+} , Mg^{2+} , and Ca^{2+}), heavy metals (Mn^{2+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cr^{3+} , Al^{3+} , Si^{4+}), and anions (acetate, sulfate, chloride, nitrate, and phosphate), which coexist in environmental water samples on the measurement of Cd (II), was investigated. In these experiments, 5.0 mL of solutions contained $0.5 \text{ } \mu\text{g mL}^{-1}$ Cd (II) and different amounts of foreign ions (analyte–foreign ion ratio for heavy metals 1:1, 1:10, 1:100 and for alkali, alkaline earth, and anions 1:100, 1:1,000, 1:2,500, and 1:5,000) were treated according to the recommended procedure. The tolerable concentration of the coexisting ions defined as the largest amount making 10% variation of the recovery of the analytes in comparison with the case in which interfering ion was absent. The obtained results are given in Table 7. Alkali and alkaline earth elements do not react to APDC because of its selectivity. However, large amounts of metal ions, which react to APDC appreciably, reduce the efficiency of Cd (II) recovery.

Table 7 Study of interfering ions

Foreign ions	Tolerable concentration (analyte/interfering ion)
Si^{4+} , As^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cr^{3+} , Al^{3+} , Fe^{3+}	1:10
Mn^{2+} , Cu^{2+}	1:100
Li^+ , Na^+ , K^+	1:5,000
Sr^{2+} , Ba^{2+} , Ca^{2+} , Mg^{2+}	1:2,500
SO_4^{2-} , H_2PO_4^- , CH_3COO^- , Cl^- , NO_3^- , PO_4^{3-}	1:5,000

Table 8 Analysis result of the five kind of environmental water samples at spiked level by the DLLME-ICP-OES

Water sample	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	Recovery (%)	RSD ^a (%)
Tap	0	nd		
	0.5	0.49	98	3.4
Mineral	0	nd		
	0.5	0.48	96	2.6
River	0	nd		
	0.5	0.47	94	4.2
Dam	0	nd		
	0.5	0.46	92	2.8
Sea	0	nd		
	0.5	0.52	104	8.5

nd not detected

^a $n = 5$

Analysis of real water samples

The efficiency of the proposed method was evaluated by determining the concentrations of cadmium in tap, mineral, river, dam, and sea water samples. All the water samples were collected in polypropylene bottles and stored at 4°C a few days before analysis. Tap water was collected from our laboratory (Tehran, Iran). Dam and river water were collected from Amir Kabir dam and Karaj River (Karaj, Iran). Sea water collocated from Caspian Sea (north of Iran). All of these water samples were firstly filtered through 0.45- μm filter and then operated according to DLLME procedure. The target analyte was not found in the real samples. Accuracy was calculated as the percentage recovery of known amounts of target analyte added to water samples and subjected to the DLLME method under the optimized conditions. The real sample analytical results and the recoveries for the spiked samples were shown in Table 8. As can be seen, the mean recoveries for the spiked real samples ranged from 92.2% to 104.5%, and the RSDs were from 2.6% to 8.5%.

Conclusion

A dispersive liquid–liquid microextraction was used for Cd (II) from water samples prior to determination by inductively coupled plasma optical

emission spectrometric technique. Experiments showed that ethanol and chloroform are the most suitable as dispersive and as extracting solvents, respectively. Two optimization methods, one variable at a time and central composite design, were applied to determine the optimum operating conditions. By using central composite design, quadratic and interaction terms between selected variables revealed. Therefore, we were able to see detailed effect of factors on each other and also on the efficiency factor, recovery, and sedimented phase volume. This helped us to choose the best experimental conditions for the effective factors more precisely with minimal experimental trials.

References

- Agency of Toxic Substances and Disease Registry (1999). Toxicological profile for cadmium. Available at <http://www.atsdr.cdc.gov/toxprofiles/tp5.html>. Accessed 1 May 2008.
- Anthemidis, A. N., Zachariadis, G. A., & Stratis, J. A. (2003). Development of an on-line solvent extraction system for electrothermal atomic absorption spectrometry utilizing a new gravitational phase separator: Determination of cadmium in natural waters and urine samples. *Journal of Analytical Atomic Spectrometry*, *18*, 1400–1403.
- Araujo, P. W., & Brereton, R. G. (1996). Experimental design II, optimization. *Trends in Analytical Chemistry*, *15*, 63–70.
- Atsumi, K., Minami, T., & Uada, J. (2005). Determination of cadmium in spring water by graphite-furnace atomic absorption spectrometry after coprecipitation with ytterbium hydroxide. *Analytical Science*, *21*, 647–650.
- Batterham, G. J., Munksgaard, N. C., & Parry, D. L. (1997). Determination of trace metals in sea-water by inductively coupled plasma mass spectrometry after off-line dithiocarbamate solvent extraction. *Journal of Analytical Atomic Spectrometry*, *12*, 1277–1280.
- Berijani, S., Assadi, Y., Anbia, M., Milani Hosseini, M. R., & Aghaee, E. (2006). Dispersive liquid–liquid microextraction combined with gas chromatography–flame photometric detection: Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. *Journal of Chromatography A*, *1123*, 1–9.
- Chen, J. R., Xiao, S. M., Wu, X. H., Fang, K. M., & Liu, W. H. (2005). Determination of lead in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction. *Talanta*, *67*, 992–996.
- Fatahi, N., Assadi, Y., Milani Hosseini, M. R., & Zeini Jahromi, E. (2007). Determination of chlorophenols

- in water samples using simultaneous dispersive liquid–liquid microextraction and derivatization followed by gas chromatography–electron-capture detection. *Journal of Chromatography A*, 1157, 23–29.
- Gemperline, P. (2006). *Practical guide to chemometrics*, 2nd ed. Boca Raton: CRC.
- Hinkelmann, K., & Kempthorne, O. (2007). *Design and analysis of experiments. Introduction to experimental design* (2nd edn, Vol. 1). Hoboken: Wiley.
- International Agency for Research on Cancer (IARC) (1997). Monographs on the evaluation of carcinogenic risks to humans. Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry. Summary of data reported and evaluation (Vol. 58). Available at <http://www.monographs.iarc.fr/ENG/Monographs/vol58/volume58.pdf>. Accessed 1 May 2008.
- Jarup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin*, 68, 167–182.
- Jarup, L., & Alfven, T. (2004). Low level cadmium exposure, renal and bone effects—the OSCAR study. *Bio-metals*, 17, 505–509.
- Jarup, L., Berglund, M., Elinder, C. G., Nordberg, G., & Vahter, M. (1998). Health effects of cadmium exposure—a review of the literature and a risk estimate. *Scandinavian Journal of Work, Environment & Health*, 24, 1–51.
- Jiang, H., Qin, Y., & Hu, B. (2008). Dispersive liquid phase microextraction (DLPME) combined with graphite furnace atomic absorption spectrometry (GFAAS) for determination of trace Co and Ni in environmental water and rice samples. *Talanta*, 74, 1160–1165.
- Li, X., Schramel, P., Wang, Z., Grill, P., Yedile, A., & Kettrup, A. (1996). Determination of trace amounts of Sb, Pb, Tl in water samples by inductively coupled plasma atomic emission spectrometry after a diantipyrylmethane-iodide third phase preconcentration. *Microchimica Acta*, 124, 171–178.
- Liang, P., & Sang, H. (2008). Determination of trace lead in biological and water samples with dispersive liquid–liquid microextraction preconcentration. *Analytical Biochemistry*, 380, 21–25.
- Lundstedt, T., Seifert, E., Abramo, L., Thelin, B., Nystrom, A., Pettersen, J., et al. (1998). Experimental design and optimization. *Chemometrics and Intelligent Laboratory Systems*, 42, 3–40. doi:10.1016/S0169-7439(98)00065-3.
- Melek, E., Tuzen, M., & Soylak, M. (2006). Flame atomic absorption spectrometric determination of cadmium (II) and lead (II) after their solid phase extraction as dibenzylidithiocarbamate chelates on Dowex Optipore V-493. *Analytica Chimica Acta*, 578, 213–219.
- Myers, R. H., & Montgomery, D. C. (2002). *Response surface methodology*. New York: Wiley.
- Ojeda, C. B., & Rojas, F. S. (2009). Separation and preconcentration by dispersive liquid–liquid microextraction procedure: A review. *Chromatographia*, 69, 11–12. doi:10.1365/s10337-009-1104-1.
- Rezaee, M., Assadi, Y., & Hosseini, M. M. (2006). Determination of organic compounds in water using dispersive liquid–liquid microextraction. *Journal of Chromatography A*, 1116, 1–9.
- Stephan, D. D., Werner, J., & Yeater, R. P. (1998). Essential regression and experimental design for chemists and engineers. MS Excel Add-in Software Package.
- Waalkes, M. P. (2003). Cadmium carcinogenesis. *Mutation Research*, 10, 107–120.
- Wuilloud, R. G., Martinis, E. M., Olsina, R. A., & Altamirano, J. C. (2008). Sensitive determination of cadmium in water samples by room temperature ionic liquid-based preconcentration and electrothermal atomic absorption spectrometry. *Analytica Chimica Acta*, 628, 41–48.
- Yamini, Y., Hejazi, L., & Mohammadi, D. E. (2003). Column system using diaion HP-2MG for determination of some metal ions by flame atomic absorption spectrometry. *Microchimica Acta*, 142, 21–25.