

## Background Corrected Dispersive Liquid-Liquid Microextraction of Cadmium Combined with Flame Atomic Absorption Spectrometry

Ghasem Karim-Nezhad,\* Mohammad Ahmadi and Behruz Zare-Dizajdizi

Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran

Um novo procedimento foi desenvolvido para microextração líquido-líquido dispersiva de cádmio antes de sua determinação por espectrometria de absorção atômica com chama. A maior dificuldade na combinação da microextração líquido-líquido dispersiva com espectrometria de absorção atômica é a alta absorção de fundo dos solventes de extração e dispersores que encobrem a absorbância do analito. A absorção de fundo foi removida trocando o solvente orgânico da fase sedimentada por um solvente aquoso. No sistema proposto, tetracloroetileno ( $C_2Cl_4$ ) e tetrahydrofurano (THF) foram usados como solventes extrator e dispersivo, respectivamente, e, como agente complexante foi usada a ditizona. Vários fatores que podem afetar o processo de extração, como solvente dispersor, solvente de extração, o volume desses solventes, tempo de extração, temperatura da solução, concentração do agente quelante e pH foram otimizados. O efeito de interferentes na recuperação de cádmio foi estudado. Os resultados mostraram que as recuperações de cádmio são quase quantitativas na presença de íons interferentes. Sob condições ótimas, os fatores de enriquecimento e de pré-concentração foram 34,5 e 26, respectivamente; as recuperações de extração e relativa foram 69% e 99%, respectivamente. O sistema mostrou-se linear no intervalo de concentração de 5 a 150  $\mu g L^{-1}$ , com limite de detecção de 1,2  $\mu g L^{-1}$  e desvio padrão relativo ( $n = 8$ ) de 2,1%. O método proposto foi aplicado com sucesso na determinação de cádmio em amostras de água.

A new procedure was developed for dispersive liquid-liquid micro extraction of cadmium prior to its determination by flame atomic absorption spectrometry. The major difficulty in combination of dispersive liquid-liquid microextraction with flame atomic absorption spectrometry is high background absorption of the extraction and disperser solvents that covers the absorbance of analyte. The background absorption was removed by changing the solvent of sedimented phase from organic to aqueous. In the proposed approach, tetrachloroethylene ( $C_2Cl_4$ ) and tetrahydroforan (THF) were used as extraction and dispersive solvents respectively. Dithizone was used as complexing agent. Several factors that may be affect on the extraction process, such as, extraction solvent, disperser solvent, the volume of extraction and disperser solvent, extraction time, temperature of solution, concentration of chelating agent and pH were optimized. The effects of common coexisting ions on the recovery of cadmium were studied. Results showed that cadmium recoveries are almost quantitative in the presence of interfering ions. Under the optimal conditions the enrichment and enhancement factors were 34.5 and 26 respectively, the extraction and relative recoveries were 69% and 99% respectively, the calibration graph was linear in the range of 5-150  $\mu g L^{-1}$ , the detection limit was 1.2  $\mu g L^{-1}$  and the relative standard deviation ( $n = 8$ ) was 2.1%. The proposed method was applied successfully for determination of trace amounts of cadmium in water samples.

**Keywords:** background corrected dispersive liquid-liquid microextraction, dithizone, cadmium, flame atomic absorption spectrometry

### Introduction

In the recent years, pollution of the environment by heavy metals has received considerable attention. Cadmium is known to damage organs such as the kidneys,

liver and lungs.<sup>1,2</sup> Cadmium is considered a non-essential and highly toxic element, with a serious cumulative effect. Its toxicity is comparable to that of arsenic and mercury but its lethal potential is higher than that of any other metallic element. Interest in the potential link between Cd and carcinogenicity has draw attention to the Cd concentration in body fluids, tissues and foods.<sup>3</sup>

\*e-mail: g.knezhad@gmail.com

However, the determination of trace elements in various samples is particularly difficult because of the complexity of matrix and the usually low concentration that these elements present in such samples, requiring sensitive instrumental techniques and a preconcentration step in order to determine them.<sup>4</sup>

In 2006, Assadi and co-workers<sup>17</sup> developed a novel liquid-phase microextraction technique, named dispersive liquid-liquid microextraction (DLLME). This method is a miniaturized LLE that uses microliter volumes of extraction solvent and based on a ternary component solvent system in which the extraction solvent and disperser solvent are rapidly injected into the aqueous sample by syringe. The mixture is then gently shaken and a cloudy solution (water/disperser solvent/extraction solvent) was formed in the test tube. After centrifugation, the fine particles of extraction solvent were sedimented in the bottom of the conical test tube and analyzed by analytical instruments. The advantages of DLLME method are simplicity of operation, rapidity, low cost, high-recovery, high enrichment factor, and environmental benignity, with wide application prospects in trace analysis.<sup>5-18</sup>

Flame atomic absorption spectrometry (FAAS) is the most commonly used technique for the determination of metal ions extracted by DLLME. Flame atomic absorption spectrometry in addition to the advantages such as availability, simplicity of use, speed, precision and the accuracy of the technique is very compatible with DLLME due to need to low volume of sample. However, the major difficulty in combination of DLLME with flame atomic absorption spectrometry is high background absorption of extraction and disperser solvents that covers the absorbance of analyte. In this work, we developed a new procedure to solve this problem. The background absorption was removed by changing the solvent of sedimented phase from organic to aqueous.

## Experimental

### *Apparatus*

A PG-990 (PG instrument, United Kingdom) atomic absorption spectrometer equipped with deuterium background correction and cadmium hollow cathode lamp was used for determination of cadmium at wavelength of 228.8 nm according to instrument instruction. The instrumental parameters were adjusted according to the manufacturer's recommendations. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal. The

pH values were measured with a Metrohm pH-meter (Model: 691Herisau, Switzerland), supplied with a glass-combined electrode. Phase separation was assisted using a centrifuge (Hettich) in 15 mL calibrated centrifuge tubes (Superior, Germany).

### *Reagents and solutions*

All chemicals were analytical-reagent grade and all solutions were prepared with ultra pure water. A stock solution of 1000.0 mg L<sup>-1</sup> of cadmium ion was prepared by dissolving appropriate amounts of CdCl<sub>2</sub> (Merck, Darmstadt, Germany). Working standard solutions were prepared by serial dilutions of the stock solution with ultrapure water prior to analysis. The chelating agent, 1×10<sup>-3</sup> mol L<sup>-1</sup> dithizone (Merck, Darmstadt, Germany) was prepared daily by dissolving appropriate amount of this reagent in tetrahydroforan (Merck, Darmstadt, Germany). A solution of 3 mol L<sup>-1</sup> nitric acid (Merck, Darmstadt, Germany) was prepared in ultra pure water. Buffer solution was prepared from 0.1 mol L<sup>-1</sup> CH<sub>3</sub>COONH<sub>4</sub> (suprapure), and HCl (suprapure) or NaOH (suprapure). All glass vessels used for the trace analysis were kept in a nitric acid solution for at least 24 h, and washed subsequently twice with ultra pure water before use.

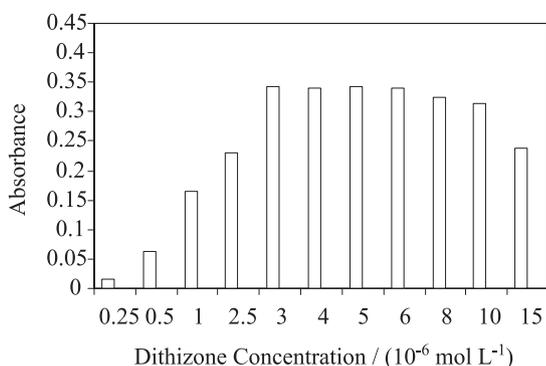
### *Dispersive liquid-liquid microextraction procedure*

10.0 mL of the sample solution containing the analyte (in the range of 5-150 µg L<sup>-1</sup>), and 3 mL ammonium acetate buffer was placed in a 15 mL screw-cap glass test tube with conical bottom. A 0.5 mL of tetrahydroforan (disperser solvent) containing 30 µL of tetrachloroethylene (extraction solvent) and 0.05 µmol dithizone (chelating agent), were injected rapidly into a sample solution using a 2 mL syringe. A cloudy solution resulting from the dispersion of the fine droplets of tetrachloroethylene in the aqueous sample was formed in the test tube. In this step, the cadmium ion reacts with dithizone and extract into the fine droplets of tetrachloroethylene. The mixture was then centrifuged at 2500 rpm for 4 min. After this process, the dispersed fine droplets of tetrachloroethylene (about 25 µL) were sedimented at the bottom of the conical test tube. The supernatant aqueous phase was then separated completely by a 5 mL syringe centered in the tube. It was added 0.2 mL of 0.5 mol L<sup>-1</sup> nitric acid in to sedimented phase and then heated at 90 °C for 3 min until the organic solvents (extraction and disperser solvents extracted to sediment phase) were evaporated completely. About 200 µL aqueous solution containing extracted cadmium was analyzed by flame atomic absorption spectrometry.

## Results and Discussion

### Effect of dithizone concentration

Dithizone is a strong ligand for metal ion extraction because it can form stable complexes with many metal ions under proper conditions. In this research, the influence of the dithizone concentration on the absorbance of cadmium ion was studied in the range of  $0.25 \times 10^{-6}$  -  $15 \times 10^{-6}$  mol L<sup>-1</sup>. The results are shown in Figure 1. The absorption was increased by increasing the dithizone concentration, which is well expected. For 100 µg L<sup>-1</sup> of cadmium, high absorbance was achieved above a dithizone concentration of  $3 \times 10^{-6}$  mol L<sup>-1</sup>. It seems that slight reduction of extraction in high concentration of dithizone is due to the extraction of dithizone itself, which can easily saturate the small volume of extraction solvent. A concentration of  $5 \times 10^{-6}$  mol L<sup>-1</sup> dithizone was chosen for the cadmium determination to prevent any interference.



**Figure 1.** Effect of dithizone amount on the absorbance of cadmium obtained from DLLME. Extraction conditions: sample volume, 10.0 mL; concentration of cadmium, 100 µg L<sup>-1</sup>; extraction solvent (C<sub>2</sub>Cl<sub>4</sub>) volume, 30 µL; disperser solvent (THF) volume, 0.50 mL.

### Background correction

The organic solvents in sedimented phase make high background absorption at flame atomic absorption spectrometry that covers the analyte signal. Thereby removing background absorption with auto zero software was impossible. For solving this problem, we tested three ways. (i) First we evaporated the organic solvents from sedimented phase by heating at 90 °C for 3 min. After solvent evaporating was completed, the solid residue was dissolved in 0.2 mL of 0.5 mol L<sup>-1</sup> nitric acid and the resultant solution was introduced into the flame. In this case, zero absorbance obtained for background and analyte. (ii) The solid residue obtained in (i), was dissolved in 50 µL of acetone and then 0.2 mL of 0.5 mol L<sup>-1</sup> nitric acid was

added. But the obtained absorbance was also zero. In last two methods, although the background absorption has been removed, the absorbance of analyte is also omitted. It seems that in these two methods, at evaporating step, cadmium ions are reduced by dithizone and stuck to the walls of the test tube. (iii) In this way, 0.2 mL of 0.5 mol L<sup>-1</sup> nitric acid (strong oxidizing agent) was added into sedimented phase and then heated at 90 °C for 3 min until the organic solvents (extraction and disperser solvents extracted to sediment phase) were evaporated completely. In this case, good absorbance signals for cadmium were obtained without any background signal.

Instead of nitric acid, hydrochloric acid was also investigated. The results demonstrated that in this case, particles of released dithizone were formed that can obstruct the aspirator tube of FAAS instrument. These particles were rapidly decomposed when nitric acid was used. To obtain optimum concentration of nitric acid, different concentrations of nitric acid in the range of 0.1-3 mol L<sup>-1</sup> were tested. Results revealed that in the concentrations below 0.5 mol L<sup>-1</sup> nitric acid, decomposition of released dithizone particles is occurred very slowly. Thereby 0.5 mol L<sup>-1</sup> of nitric acid was chosen as optimum.

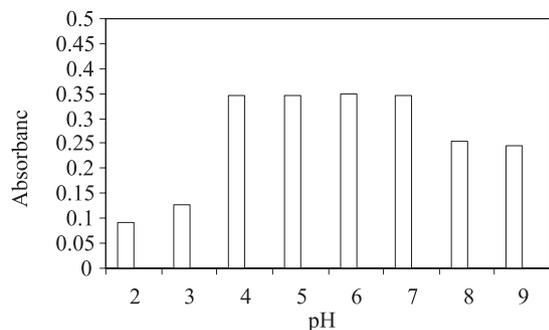
### Effect of pH

pH plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of cadmium from water samples was studied in the range of 2-9. Figure 2 reveals that the absorbance is nearly constant in the pH range of 4-7. The pH 5 was selected for the following experiments. To adjust the pH, buffers such as phosphate, acetate and ammonium acetate was tested. Results showed that ammonium acetate is better.

### Effect of extraction solvent type and volume

Extraction solvent must be immiscible with water and the solubility of analytes in this solvent should be higher than the donor phase to promote the extraction of the analytes and in the case of DLLME, the extracting solvent must have a density higher than that of the aqueous sample.

Carbon disulfide, carbon tetrachloride, chloroform, chlorobenzene and tetrachloroethylene were studied as extraction solvent. A series of sample solutions were studied by using 0.5 mL of tetrahydroforan containing 0.05 µmol of dithizone and different volumes of the extraction solvents to achieve a 25 µL volume of the sedimented phase. Since the capacity of the sediment phase is low, decreasing or increasing the volume of



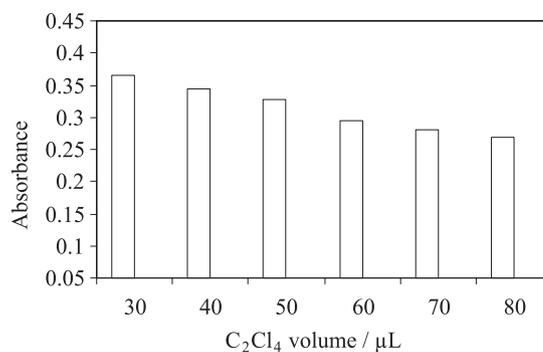
**Figure 2.** Effect of pH on the absorbance of cadmium obtained from DLLME. Extraction conditions: sample volume, 10.0 mL; concentration of cadmium,  $100 \mu\text{g L}^{-1}$ ; extraction solvent ( $\text{C}_2\text{Cl}_4$ ) volume, 30  $\mu\text{L}$ ; disperser solvent (THF) volume, 0.50 mL; dithizone amount, 0.05  $\mu\text{mol}$ .

the sediment phase may change the amount of extracted analyte. Three replicate tests were performed for each of these solvents under the same conditions. The solubility of the extraction solvents in water is different. Therefore to recover 25  $\mu\text{L}$  volume of the sedimented phase at the bottom of the test tube, it is necessary to add an excess to account for this solubility. Thereby, 50, 34, 75, 40 and 30  $\mu\text{L}$  of carbon disulfide, carbon tetrachloride, chloroform, chlorobenzene and tetrachloroethylene were used, respectively. In this experiment carbon disulfide, carbon tetrachloride, chloroform, chlorobenzene and tetrachloroethylene as extraction solvents obtained average absorbance of 0.328, 0.345, 0.283, 0.304 and 0.365 respectively. According to these results, tetrachloroethylene forms a stable cloudy solution. On the other hand it has a high absorbance and less consumption volume due to its low solubility. Therefore, it was the best to be used.

To examine the effect of the extraction solvent volume, solutions containing different volumes of tetrachloroethylene were subjected to the same DLLME procedures. The experimental conditions were fixed and included the use of 0.5 mL of tetrahydroforan containing 0.05  $\mu\text{mol}$  of dithizone and different volumes of tetrachloroethylene (30, 40, 50, 60, 70 and 80  $\mu\text{L}$ ). By increasing the volume of tetrachloroethylene from 30 to 80  $\mu\text{L}$ , the volume of the sedimented phase increases from 25 to 75  $\mu\text{L}$ . Figure 3 shows the curve of absorbance *versus* volume of the extraction solvent (tetrachloroethylene). According to Figure 3 the absorbance diminishes with increasing the volume of tetrachloroethylene, because the volume of disperser solvent is not enough to disperse the extraction solvent completely. Consequently, a high absorbance was obtained at low volumes of the extraction solvent. In the subsequent studies, 30  $\mu\text{L}$  tetrachloroethylene was used as the optimum volume of the extraction solvent.

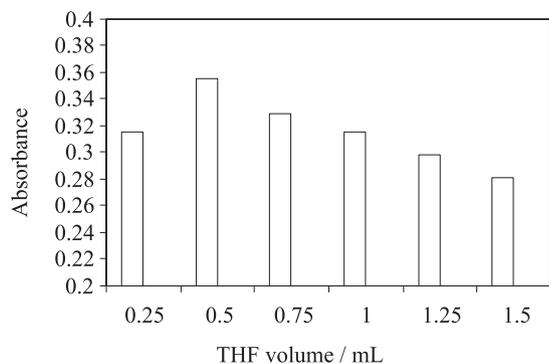
### Effect of disperser solvent type and volume

The main criterion for selection of the disperser solvent is its miscibility in the extraction solvent and aqueous sample. For this purpose, different solvents such as acetonitrile, acetone, methanol, ethanol and tetrahydroforan were tested. A series of sample solutions were studied by using 0.5 mL of each disperser solvent containing 30  $\mu\text{L}$  of tetrachloroethylene and 0.05  $\mu\text{mol}$  of dithizone. The average absorbance obtained for acetonitrile, acetone, ethanol, methanol and tetrahydroforan were 0.322, 0.297, 0.314, 0.282 and 0.355 respectively. The results show no statistical significant differences between disperser solvents; however, the solubility of dithizone (chelating agent) in tetrahydroforan makes it a better choice.



**Figure 3.** Effect of the volume of extraction solvent ( $\text{C}_2\text{Cl}_4$ ) on the absorbance of cadmium obtained from DLLME. Extraction conditions are the same with Figure 2; pH = 5.

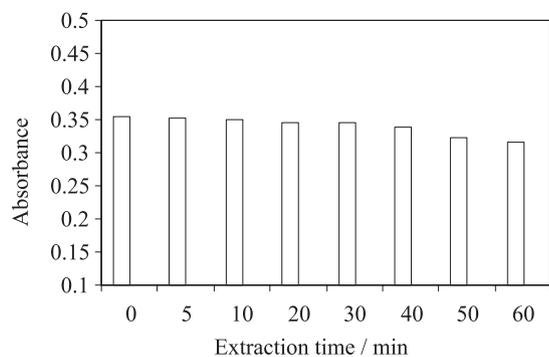
The effect of tetrahydroforan volume on the extraction efficiency was also studied. Since variation of tetrahydroforan volume may change the volume of sedimented phase, thereby, to avoid this and in order to achieve a constant volume of sediment phase (25  $\mu\text{L}$ ), the volume of tetrahydroforan and tetrachloroethylene were changed simultaneously. The experimental conditions were fixed and included the use of different volumes of tetrahydroforan 0.25, 0.50, 0.75, 1, 1.25 and 1.50 mL containing 0.05  $\mu\text{mol}$  dithizone and 29, 30, 31, 32, 33 and 34  $\mu\text{L}$  of tetrachloroethylene, respectively. Under these conditions, the volume of the sedimented phase was constant ( $25 \pm 1 \mu\text{L}$ ). Figure 4 shows the curves of absorbance of cadmium versus the volume of tetrahydroforan. At low volume (0.25 mL), tetrahydroforan cannot disperse extraction solvent properly and cloudy solution is not formed completely. At high volumes (0.75-1.5 mL) the extraction efficiency decreases due to increasing the solubility of tetrachloroethylene in water. According to the results, a 0.50 mL tetrahydroforan was chosen as the optimum volume.



**Figure 4.** Effect of the volume of tetrahydroforan on the absorbance of cadmium obtained from DLLME. Extraction conditions are the same with Figure 3.

#### Effect of the extraction time

In DLLME, extraction time is defined as interval time between injection the mixture of disperser solvent (THF) and extraction solvent (tetrachloroethylene), before starting to centrifuge. The influence of the extraction time was evaluated in the range of 0-60 min with constant experimental conditions. Figure 5 shows that the extraction time has no significant effect on the extraction efficiency. It was revealed that after the formation of the cloudy solution, the surface area between the extraction solvent and the aqueous phase is infinitely essentially large. Thereby, complex formation of cadmium and its transfer from the aqueous phase to the extraction solvent is fast. This is one of the considerable advantages demonstrated by the DLLME technique. In this method, the most time-consuming steps are the centrifuging of cloudy solution (about 4 min) and evaporating of solvents (about 3 min).



**Figure 5.** Effect of extraction time on the absorbance of cadmium obtained from DLLME. Extraction conditions are the same with Figure 3.

#### Effect of temperature

Temperature is another parameter that may have an effect on extraction efficiency. In order to examine this impact, extraction procedures were done in the range of

25-65 °C. The results obtained from these tests showed that by increasing the temperature from 45 to 65 °C, absorbance of cadmium is decreased, because increasing temperature increases the solubility of extraction solvent in aqueous solution, also dithizone decomposes and other reason was rapidly evaporating disperser solvent (THF). According to these results, laboratory temperature (25 °C) is suitable for doing the extraction procedure.

#### Effect of ionic strength

To investigate the influence of ionic strength on DLLME performance, various experiments were performed by adding different amounts of NaCl (0-5%, m/v). The experimental conditions were kept constant. By increasing the NaCl from 0 to 5%, the absorbance of cadmium decreases slightly. Probably, the formation of  $\text{CdCl}_4^{2-}$  at high concentration of NaCl decreases the formation of Cd-dithizone that can be extracted into organic phase. On the other hand, salting-out effect increases the extraction recovery. It seems these phenomenas make an opposite effect. Therefore, the extraction recovery is nearly constant by increasing the amount of sodium chloride.

#### Extraction recovery

Extraction recovery is important factor in DLLME because it has a major effect on the enrichment factors. Compared with the conventional solvent extraction, microextraction may provide poor analyte recovery; instead, the concentration in the organic phase is greatly enhanced. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary; therefore, problems of contamination and loss of analytes vanish.<sup>19</sup> To study the extraction recovery of the proposed method, replicated extractions from one solution were used. This experiment performed with two concentration levels. The results are given in Table 1. According to the obtained results, the extraction recovery is approximately 69% and comparable with those reported in literatures.<sup>16</sup> The relative recovery was also obtained that is almost 99%.

#### Effect of coexisting ions

The effects of common coexisting ions in natural water samples on the recovery of cadmium were studied. In these experiments, 10.0 mL of solutions contains  $100 \mu\text{g L}^{-1}$  of cadmium and various amounts of interfering ions were treated according to the recommended procedure. A given spices was considered to interfere if it resulted in a  $\pm 5\%$  variation of the AAS signal. The obtained results are given in Table 2

**Table 1.** Extraction recovery of cadmium using DLLME-FAAS

Cadmium concentrations / ( $\mu\text{g L}^{-1}$ )	Extraction recovery / (%)		
	1 <sup>st</sup> Extraction	2 <sup>nd</sup> Extraction	3 <sup>rd</sup> Extraction
50	69.37	20.62	9.91
100	68.26	21.10	10.45

**Table 2.** Effect of interferents on the recovery of  $100 \mu\text{g L}^{-1}$  cadmium in water sample by using DLLME-FAAS. Conditions were the same as Figure 3

Interferent	Interferent / Cd ratio	Recovery / (%)
K+	10,000	99.4
Na+	10,000	99.7
Ca(II)	1000	100.2
Mg(II)	1000	98.6
Al(III)	500	99.7
Mn(III)	500	99.1
Fe(III)	500	98
Co(II)	500	80.8
	100	99.7
Ni(II)	500	83.3
	100	100.2
Pb(II)	500	90.7
	100	99.2
Zn(II)	500	88.7
	100	98.6
Cu(II)	500	83.9
	100	98.3

and prove that the cadmium recoveries are almost quantitative in the presence of the described ratios of interfering cations.

#### Characteristics of the method

Under the optimum conditions described above, the analytical performance characteristics of the proposed method are listed in Table 3. The aqueous calibration curve was linear in the concentration range  $5\text{--}150 \mu\text{g L}^{-1}$  of cadmium. The limit of detection, defined as  $\text{LOD} = 3S_B/m$  (where LOD,  $S_B$  and  $m$  are the limit

**Table 3.** Analytical characteristics of DLLME-FAAS for determination of cadmium

Parameter	Analytical feature
Equation of the calibration graph <sup>a</sup>	$Y = 0.0026x + 0.0803$
Linear range / ( $\mu\text{g L}^{-1}$ )	5-150
$r^2$	0.9997
Limit of detection / ( $\mu\text{g L}^{-1}$ ) (3 $\sigma$ , n = 8)	1.2
RSD / (%) (n = 8, $100 \mu\text{g L}^{-1}$ )	2.1
Enrichment factor <sup>b</sup>	34.5
Enhancement factor	26
Sample volume / mL	10
Sample preparation time / min	7

<sup>a</sup>y, is absorbance of cadmium and x, is concentration of cadmium ( $\mu\text{g L}^{-1}$ ); <sup>b</sup>the enrichment factor defined as  $\text{EF} = C_f/C_0$ ; <sup>c</sup>enhancement factor is calculated as the ratio of slope of proposed DLLME method to that obtained without preconcentration

of detection, the standard deviation of the blank and the slope of the calibration graph, respectively) was  $1.2 \mu\text{g L}^{-1}$ . The relative standard deviation (RSD) for eight replicate measurements of  $100 \mu\text{g L}^{-1}$  cadmium was 2.1%. The enhancement factor, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, was about 26. The enrichment factor defined as  $\text{EF} = C_f/C_0$ , where EF,  $C_f$  and  $C_0$  are the enrichment factor, concentration of analyte in final phase and initial concentration of analyte in aqueous sample, respectively. This factor was obtained about 34.5.

Some characteristics of previously reported methods such as enrichment factor, RSD% and LOD are summarized in Table 4 for comparison. As can be seen, the proposed DLLME method, for preconcentration of cadmium, shows good enrichment factor, short extraction procedure and better RSD% in most cases to the previously reported methods.

#### Natural water analysis

To test the reliability of the recommended procedure, the method was applied to the determination of cadmium in tap,

**Table 4.** Comparison of the proposed method with other reported methods for preconcentration of cadmium

System	Analysis method	Sample volume / mL	Sample preparation time / min	Enrichment factor	RSD / (%)	Linear range / ( $\text{ng L}^{-1}$ )	LOD / ( $\text{ng L}^{-1}$ )	Ref
On-line solvent extraction	GFAAS	14.0	2	24.6	3.2	6-300	2.8	20
Co-precipitation	GFAAS	100.0	> 30	100	3.2	100-4000	2.9	21
On-line SPE	GFAAS	3.0	4	59.4	1.3	20-200	1.3	22
CPE	GFAAS	10.0	> 30	50	2.1	0-20	5.9	23
SDME	GFAAS	5.0	> 10	65	7.4	10-1000	0.7	24
DLLME	GFAAS	10.0	2	67	3.3	20-150	7.4	25
DLLME	GFAAS	5.0	< 3	125	3.5	2-20	0.6	2
CPE	FAAS	10.0	20	-	2.4	$1\text{--}100 \mu\text{g L}^{-1}$	$0.31 \mu\text{g L}^{-1}$	1
DLLME	FAAS	10.0	7	34.5	2.1	$5\text{--}150 \mu\text{g L}^{-1}$	$1.2 \mu\text{g L}^{-1}$	Present work

**Table 5.** Determination of cadmium in tap, well, river, and rainwater samples and relative recovery of spiked cadmium in tap, well, river and rainwater samples

Sample	Added Cd / ( $\mu\text{g L}^{-1}$ )	Found Cd / ( $\mu\text{g L}^{-1}$ ) mean $\pm$ SD <sup>a</sup>	Relative recovery / (%)
Tap water <sup>b</sup>	-	N.D. <sup>f</sup>	-
	50	49.60 $\pm$ 0.8	99.2
Well water <sup>c</sup>	-	N.D. <sup>f</sup>	-
	50	48.95 $\pm$ 1	97.9
River water <sup>d</sup>	-	N.D. <sup>f</sup>	-
	50	49.85 $\pm$ 1.2	99.7
Rainwater <sup>e</sup>	-	N.D. <sup>f</sup>	-
	50	49.8 $\pm$ 0.9	99.6

<sup>a</sup>Standard deviation (n = 3); <sup>b</sup>from drinking water system of khoy, Iran; <sup>c</sup>from khoy, Iran; <sup>d</sup>river water, from khoy, Iran; <sup>e</sup>From khoy, Iran(September 20, 2010); <sup>f</sup>not detected.

well, river and rainwater samples. For this purpose, a volume of 10.0 mL of each sample was preconcentrated with 0.5 mL of tetrahydroforan contains 30  $\mu\text{L}$  of tetrachloroethylene and 0.05  $\mu\text{mol}$  of dithizone. The accuracy of the method was verified by the analysis of the samples spiked with known cadmium amounts. The relative cadmium recoveries from tap, well, river and rainwater at the spiking level of 50  $\mu\text{g L}^{-1}$  were 99.2, 97.9, 99.7 and 99.6 %, respectively (Table 5). These results demonstrated that the matrices of the tap, well, river and rainwater samples had little effect on the DLLME method for determination of cadmium.

## Conclusions

A new procedure was developed for dispersive liquid-liquid micro extraction of cadmium prior to its determination by flame atomic absorption spectrometry. The high background absorption of the extraction and disperser solvent was removed by changing the solvent of sedimented phase from organic to aqueous. From the obtained results it can be considered that dithizone is an efficient ligand for dispersive liquid-liquid microextraction of cadmium. The simple accessibility, the formation of stable complexes and consistency with the dispersive liquid-liquid microextraction method are the major advantages of the use of dithizone in dispersive liquid-liquid microextraction of cadmium. The proposed method offers a simple, sensitive and inexpensive alternative to other separation/preconcentration techniques.

## Acknowledgments

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