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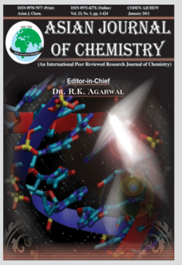

Preconcentration and Determination of Ultratrace of Cd(II) in Water Samples Using Dispersive Liquid-Liquid Microextraction with N-Benzoyl-N-phenylhydroxylamine

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Dispersive liquid-liquid microextraction (DLLME) technique was successfully used as a sample preparation method for graphite furnace atomic absorption spectrometry (GF AAS). In this extraction method, 500 µL methanol (disperser solvent) containing 34 µL carbon tetrachloride (extraction solvent) and 0.00010 g N-benzoyl-N-phenylhydroxylamine was rapidly injected by syringe into the water sample containing cadmium ions. A cloudy solution is formed. The cloudy state resulted from the formation of fine droplets of carbon tetrachloride, which have been dispersed, in bulk aqueous sample. At this stage, cadmium reacts with N-benzoyl-N-phenylhydroxylamine and therefore, hydrophobic complex forms which is extracted into the fine droplets of carbon tetrachloride. After centrifugation (2 min at 5000 rpm), these droplets were sedimented at the bottom of the conical test tube (25 ± 1 µL). Then a 20 µL of sedimented phase containing enriched analyte was determined by GF AAS. Some effective parameters on extraction and complex formation, such as extraction and disperser solvent type and their volume, extraction time, salt effect, pH and concentration of the chelating agent have been optimized. Under the optimum conditions, the enrichment factor 118 was obtained from only 5.00 mL of water sample. The calibration graph was linear in the rage of 2-21 ng L^{-1} with detection limit of 0.6 ng L^{-1}. The relative standard deviation (RSDs) for ten replicate measurements of 20 ng L^{-1} of cadmium was 3.1 %. The relative recoveries of cadmium in tap, sea and rain water samples at spiking level of 5 and 10 ng L^{-1} are 98, 94, 96 and 93 %, respectively. The characteristics of the proposed method have been compared with cloud point extraction, on-line liquid-liquid extraction, single drop microextraction, on-line solid phase extraction and co-precipitation based on bibliographic data. Therefore, dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry is a very simple, rapid and sensitive method, which requires low volume of sample (5.00 mL).

Key Words: Dispersive liquid-liquid microextraction, Cadmium, Graphite furnace atomic absorption spectrometry, Water analysis.

INTRODUCTION

In the recent years, pollution of the environment by heavy metals has received considerable attention. These elements accumulate in living organisms and are of high toxic potential. Their wide technological use (fertilizers, mining, pigments), as well as their production from burning oil and coal and incineration of waste causes an extensive anthropogenic contamination of soil, air and water[1]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS)[2,3], inductively coupled plasma atomic emission spectrometry (ICP-AES)[4] and inductively coupled plasma mass spectrometry (ICP-MS)[5] are available for the determination of trace metals with enough sensitivity for the most applications.

Despite good developments in the modern analytical instruments, which allow great enhancement in aspects of analysis, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples.

Sample preparation is still a bottleneck for overall throughput because the involved steps often employ large volumes of hazardous organic solvents, are time consuming and/or expensive[1]. Although, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrices effects. Pre-concentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace elements. Several procedures have been developed for the separation and preconcentration of contaminants from environmental matrices,such as: liquid-liquid extraction (LLE)[6-8], co-precipitation[9-11], solid phase extraction (SPE)[12-20].

Although, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption, limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100[1]. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances. 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 vanishes.

Cloud point extraction (CPE)[21-26], homogeneous liquid-liquid extraction (HLLE)[27,28] and single drop microextraction (SDME)[29-33] are fairly new methods of sample preparation which are used in separation and preconcentration of metals and can solve some of the problems encountered with the conventional pretreatment techniques.

In the previous researches, we demonstrated a novel microextraction technique, named dispersive liquid-liquid microextraction (DLLME), which was successfully used, for the extraction and determination of polycyclic aromatic hydrocarbons, organphosphorus pesticides and chlorobenzenes in water samples[34-36]. Dispersive liquid-liquid microextraction is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods. In dispersive liquid-liquid microextraction, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of anlaytes in sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

Dispersive liquid-liquid microextraction is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a microamount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GF AAS is used. The applicability of the approach has been demonstrated for the determination of cadmium in water samples. This element was selected for evaluation of the procedure because cadmium is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations[37,38].

EXPERIMENTAL

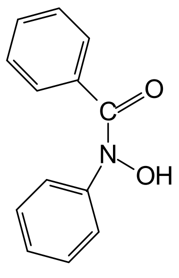
The experiments were performed using a Shimadzu (Kyoto, Japan) atomic absorption spectrophotometer (AA 6300G) with a graphite furnace atomizer (GFA-EX7i). A cadmium hollow cathode lamp (Hamamatsu Photonics, Shizaoka, Japan), operated at a current of 8 mA and a wavelength of 228.8 nm with a spectral band pass of 0.7 nm was used. Pyrolytically coated graphite tubes (Shimadzu) were used. The sample injection volume was 20 μL in all experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table-1. The good wetting of graphite by organic solvents promotes its penetration by the extracts that may give rise to signals of complicated shape. To prevent this undesirable effect, organic extracts can be added to electrothermal atomizer heated to the drying temperature and this will also prevent sample from spreading over the atomizer surface[39]. Therefore 20 μL of the sedimented phase was introduced into the graphite furnace after 10 s starting the drying step in all experiments. Argon 99.999 % purchased from Air Products (West Sussex, UK) as sheath gas. The Centurion Scientific centrifuge (Model 1020D, UK) was used for centrifuging. The pH values were measured with a Metrohm pH meter (Model: 691, Herisau, Switzerland) supplied with a glass-combined electrode.

TABLE-1
GRAPHITE FURNACE TEMPERATURE PROGRAM FOR CADMIUM DETERMINATION

Argon flow rate (mL min^{-1})	Hold time (s)	Ramp time (s)	Temperature (ºC)	Step
250	20	1	70	Drying
250	10	5	200	Pyrolysis
0	4	0	2200	Atomization
1000	2	0	2400	Cleaning

All solutions were prepared using ultra pure water (Ghazi Co., Tabriz, Iran). The stock solution of cadmium (1000 mg L^{-1} for atomic spectroscopy standard) was purchased from Merck (Darmstadt, Germany). Working standard solutions were prepared by serial dilutions of the stock solution with ultra pure water prior to analysis. The chelating agent, 0.020 g L^{-1} N-benzoyl-N-phenylhydroxylamine (BPHA) solution, was prepared daily by dissolving the appropriate amount of BPHA (BPHA was prepared according to the procedure described by Takeshima *et al.*[40]) in methanol (suprasolv, Merck).

Other chemicals used were: carbon tetrachloride (analytical grade for determination with dithizone), chloroform (analytical grade for determination with dithizone) and carbon disulfide (for spectroscopy) as extraction solvent, ethanol (for spectroscopy), acetone (suprasolv) and acetonitrile (HPLC grade) as disperser solvent, HNO_3 (65 %, suprapur), CH_3COONa (suprapur) and Na_2HPO_4 (suprapur) were obtained from Merck. The NaCl solutionwas prepared by dissolving the appropriate amount of NaCl (analytical grade, Merck) in ultrapure water and was extracted by carbon tetrachloride in the presence of BPHA for further purification. All glass vessels used for trace analysis were kept in 0.1 % solution of BPHA for at least 24 h and subsequently washed twice with ultrapure water and twice with acetone before use. Tap, sea and rivers water samples used for development of the method were collected in PTFE containers from the North of Iran and added appreciated amount of HNO_3 to adjust pH 3 and stored in dark at 4 ºC and analyzed within 48 h of collection without previous treatment or filtration.



Structure of N-benzoyl-N-phenylhydroxylamine

Dispersive liquid-liquid microextraction procedure: A 5.00 mL of ultrapure water contains 50 μL HNO_3 (0.1 N, suprapur) was placed in a 10 mL screw cap glass test tube with conic bottom and spiked at levels of 20 ng L^{-1} of cadmium. Five hundred microliters of methanol (disperser solvent) contains 34 μL of carbon tetrachloride (extraction solvent) and 0.00010 g of BPHA (chelating agent) was injected rapidly into a sample solution by using 0.50 mL syringe (gastight, Hamilton, Reno, Nevada, USA). A cloudy solution (water, methanol and carbon tetrachloride) was formed in a test tube. In this step, cadmium ions react with BPHA and extract into the fine droplets of carbon tetrachloride. The mixture was then centrifuged for 2 min at 5000 rpm. After this process the dispersed fine droplets of carbon tetrachloride were sedimented at the bottom of conical test tube (25 ± 1 μL). Twenty microliters of this sedimented phase was removed using a sampler (eppendorf, Hamburg, Germany) and injected into graphite furnace atomic absorption spectrometer. The volume of the sedimented phase was determined using a 50 μL microsyringe, which was about 25 μL.

RESULTS AND DISCUSSION

In this studies, DLLME combined with GF AAS was developed for the first time. Cadmium was chosen as an example to study the possibility of this combination. In order to obtain a high enrichment factor, the effect of different parameters affecting the complex formation and extraction conditions, such as kind of extraction and disperser solvent and their volume, pH, concentration of the chelating agent, extraction time and salt addition were optimized. Eqn. 1 was used for calculation of the enrichment factor.

$$\text{Enrichment factor (EF)} = \frac{C_{sed}}{C_0} \quad (1)$$

where EF, C_{sed} and C_0 are the enrichment factor, concentration of the analyte in the sedimented phase and initial concentration of the analyte in the aqueous sample, respectively. C_{sed} was calculated from the calibration graph obtained by conventional LLE-GF AAS (extraction conditions: 5.00 mL standard water sample in the concentration range of 0.5-3.0 μgL^{-1} of Cd, 5.00 mL CCl_4, 0.0050 g BPHA and pH = 3).

Effect of type and volume of the extraction solvent: Careful attention should be paid to the selection of the extraction solvent. It should have higher density rather than water, extraction capability of the interested compounds and low solubility in water. Chloroform, carbon tetrachloride and carbon disulfide were compared in the extraction of cadmium. A series of sample solution were studied by using 500 μL methanol containing 0.00010 g of BPHA and different volumes of the extraction solvent to achieve 25 μL volume of the sedimented phase. The solubility of the extraction solvents in water is different. Therefore to recover 25 μL 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, 75, 50 and 34 μL of chloroform, carbon disulfide and carbon tetrachloride were used, respectively.

In this experiment chloroform, carbon disulfide and carbon tetrachloride as extraction solvents obtained enrichment factors of 128.9 ± 8.6, 122.1 ± 11.5 and 118.7 ± 6.4, respectively. According to these results, variations of the enrichment factors using different extraction solvents are not statistically significantly different. Carbon tetrachloride forms a well stable cloudy solution, its sedimented phase can easily be removed by sampler to be introduced into the graphite furnace and has less consumption volume, while chloroform forms an unstable cloudy solution and carbon disulfide is difficult to be removed by sampler. Therefore, carbon tetrachloride was the best to be used.

To examine the effect of the extraction solvent volume, solutions containing different volumes of carbon tetrachloride were subjected to the same DLLME procedures. The experimental conditions were fixed and include the use of 500 μL methanol containing 0.00010 g of BPHA and different volumes of carbon tetrachloride (34, 44, 54, 64, 74 and 84 μL). By increasing the volume of carbon tetrachloride from 34-84 μL, the volume of the sedimented phase increases from 25-75 μL. Using less than 34 μL volume of carbon tetrachloride decreases the volume of the sedimented phase to less than 25 μL. Therefore, removing the sedimented phase for injection into the GF AAS would be too difficult and accompany with systematic error. Fig. 1 shows the curve of enrichment factor *versus* volume of the extraction solvent (carbon tetrachloride).

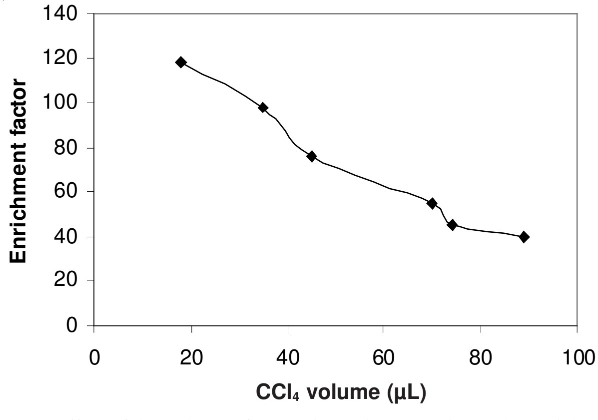


Fig. 1. Effect of the volume of extraction solvent (CCl_4) on the enrichment factor of Cd obtained from DLLME. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (methanol) volume, 0.50 mL; BPHA amount, 0.00010 g; pH 3; concentration of Cd, 20 ng L^{-1}

According to Fig. 1, enrichment factor decreases with increasing the volume of carbon tetrachloride, because of the volume of the sedimented phase increases. Subsequently, at low volume of the extraction solvent high enrichment factor was obtained. Thereby, the gain in sensitivity was achieved by using 34 μL of carbon tetrachloride.

Effect of type and volume of the disperser solvent: 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 acetone, acetonitrile, methanol and ethanol were tested. A series of sample solutions were studied by using 500 μL of each disperser solvent containing 34 μL of carbon tetrachloride (extraction solvent). Since the solubility of BPHA in acetone and acetonitrile is low, in this experiment, an aqueous solution of BPHA was prepared and added to water samples before the extraction. The enrichment factors obtained for acetonitrile, acetone, methanol and ethanol were 108.7 ± 9.1, 118.2 ± 8.8, 118.4 ± 5.3 and 115.6 ± 7.5, respectively. The results show no statistical significant differences between disperser solvents. However, the solubility of BPHA in methanol makes it a better choice.

The effect of the volume of methanol on the extraction recovery was also studied. Since, variation of the volume of methanol makes change in the volume of sedimented phase at constant volume of carbon tetrachloride (extraction solvent). Thereby, to avoid this matter and in order to achieve a constant volume of sedimented phase (25 μL) the volume of methanol and carbon tetrachloride were changed, simultaneously. The experimental conditions were fixed and include the use of different volumes of methanol 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50 mL containing 0.00010 g of BPHA and 33.0, 34.0, 35.0, 36, 37.5 and 39.0 μL of carbon tetrachloride, respectively. Under these conditions, the volume of the sedimented phase was constant (25 ± 1 μL). The results showed that there was no considerable variation on extraction efficiency by using 0.25 and 0.50 mL of methanol as disperser solvent. The extraction efficiency slightly decreased when the volume of methanol exceeded 0.50 mL. It is clear that by increasing the volume of methanol, the solubility of complex in water increases. Therefore, the extraction recovery decreases. Thus, 500 μL of methanol was selected as optimum volume in order to achieve better and more stable cloudy solution.

Effect of the extraction time: Extraction time is one of the most important factors in the most of the extraction procedure. In dispersive liquid-liquid microextraction, extraction time is defined as the time between injection mixture of disperser and extraction solvent and starting to centrifuge. The effect of extraction time was examined in the range of 0-60 min with constant experimental conditions. The results showed that the extraction time has no significant effect on the extraction efficiency. It is revealed that after formation of cloudy solution, the surface area between extraction solvent and aqueous phase (water sample) is infinitely large. Thereby, complex formation of cadmium and its transfer from aqueous phase (water sample) to extraction solvent is fast. Subsequently, equilibrium state is achieved quickly, therefore, the extraction time is very short. This is the advantage of DLLME technique, *i.e.*, short extraction time. In this method, the most time-consuming step is the centrifuging of sample solution in extraction procedure, which is about 2 min.

Effect of pH: The separation of metal ions by dispersive liquid-liquid microextraction involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of the sedimented phase, thus, obtaining the desired preconcentration. 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 1.3-8.1 by using HNO_3, CH_3COONa and Na_2HPO_4. The results illustrated in Fig. 2 reveal that the absorbance is nearly constant in the pH range of 2.8-8.0. As in low pH, cations are less likely to precipitate, pH 3 seems a proper choice. Moreover, to make pH 3 adjustment, the use of buffer (which are sources of contamination) is not necessary and nitric acid can simply be used to make the pH adjustment.

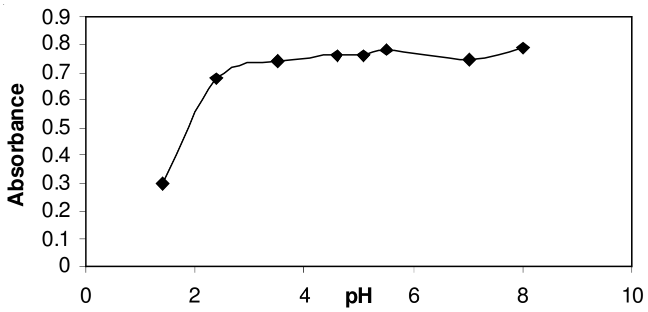


Fig. 2. Effect of pH on the absorbance of Cd obtained from DLLME. Extraction conditions, as with Fig. 1; extraction solvent (CCl_4) volume, 34 μL

Effect of BPHA concentration: The effect of the BPHA amount on the absorption is shown in Fig. 3. The absorption was increased by increasing the BPHA amount, which is well expected. It seems that slight reduction of extraction in high concentration of BPHA is due to the extraction of BPHA itself, which can easily saturate the small volume of extraction solvent. Also, at high concentration of BPHA (0.0010 g) the background absorbance was increased. Therefore, the amount of 0.00010 g of BPHA was selected as the best choice to prevent any interference.

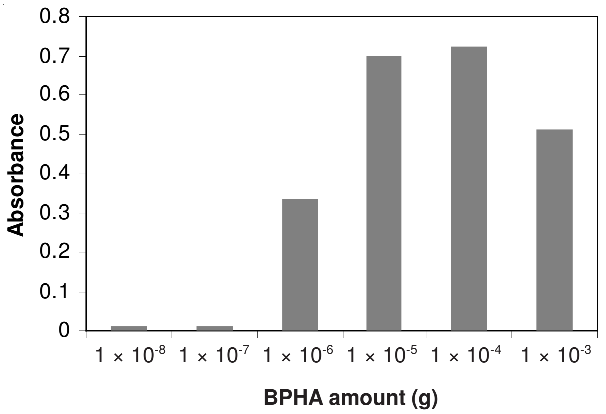


Fig. 3. Effect of BPHA amount on the absorbance of Cd obtained from DLLME. Extraction conditions, as with Fig. 2

Effect of salt: For investigating the influence of ionic strength on performance of DLLME, various experiments were performed by adding different amount of NaCl [0-5 % (w/v)]. Other experimental conditions were kept constant. By increasing the NaCl from 0-5 %, the volume of sedimented phase increases slightly from 25-28 μL. The results showed that salt addition has no significant effect on the enrichment factor. It may be because of two opposite effects of salt addition in DLLME of cadmium. One of them is increasing the volume of sedimented phase that decreases the enrichment factor and another is salting-out effect that increases the enrichment factor. Therefore, the enrichment factor is nearly constant by increasing the amount of sodium chloride. These observations showed the possibility of using this method for separation of cadmium from saline solutions up to 5 %.

Effect of coexisting ions: The effects of common coexisting ions in natural water samples on the recovery of cadmium were studied. In these experiments, 5.00 mL of solutions contains 20 ng 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 ± 5 % variation of the AAS signal. The results obtained are given in Table-2.

TABLE-2
EFFECT OF INTERFERENTS ON THE RECOVERY OF 20 ng L^{-1} Cd(II) IN WATER SAMPLE USING DLLME-GF AAS

Recovery (%)	Interferent/Cd(II) ratio	Concentration (μg L^{-1})	Interferent
94.3	200,000,000	40,00,000	Na^+
100.2	10,000	200	Li^+
98.5	10,000	200	K^+
99.4	10,000	200	Ca^{2+}
99.7	10,000	200	Mg^{2+}
98.5	10,000	200	Ba^{2+}
100.6	10,000	200	Sr^{2+}
94.7	10,000	200	Mn^{2+}
98.8	10,000	200	Co^{2+}
97.2	10,000	200	Al^{3+}
98.5	10,000	200	Fe^{3+}
65.6	10,000	200	Ni^{2+}
98.7	1000	20	–
51.8	10,000	200	Zn^{2+}
93.9	1000	20	–
72.4	10,000	200	Pb^{2+}
100.3	1000	20	–
73.0	10,000	200	Fe^{2+}
98.5	1000	20	–
69.4	10,000	200	Cu^{2+}
85.7	1000	20	–
96.8	100	2	–
67.3	10,000	200	Cr^{3+}
99.5	1000	20	–
93.7	10,000	200	Cr^{6+}
69.4	10,000	200	As^{3+}
98.8	1000	20	–
97.4	10,000	200	As^{5+}
25.6	10,000	200	Hg^{2+}
70.1	1000	20	–
92.7	100	2	–
94.6	300,000,000	60,00,000	Cl^-
102.7	10,000	200	NO_3^-
99.3	500,000,000	10,000,000	CH_3COO^-
98.6	500,000,000	10,000,000	$H_2PO_4^-$

Figures of merit: Table-3 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility and enhancement factor. The calibration graph was linear in the range of 2-21 ng L^{-1} of cadmium. The limit of detection, defined as $C_L = 3\ S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.6 ng L^{-1}. The relative standard deviation (RSD) for ten replicate measurements of 20 ng L^{-1} Cd(II) was 3.4 %. The enhancement factor was obtained from the slope ratio of calibration graph after and before extraction, which was about 100.

TABLE-3
ANALYTICAL CHARACTERISTICS OF DLLME-GF AAS FOR DETERMINATION OF CADMIUM

Analytical feature	Parameter
2–21	Linear range (ng L^{-1})
0.9993	r^2
0.6	Limit of detection (ng L^{-1}) (3σ, n = 10)
3.4	Repeatability (RSD[a], %) (n = 10)
118	Enrichment factor
100	Enhancement factor[b]
5.00	Sample volume (mL)
< 4	Extraction time (min)

[a] Cd(II) concentration was 20 ng L^{-1} for which RSD was obtained.
[b] Enhancement factor is the slope ratio of calibration graph after and before extraction.

Analysis of natural waters: The proposed DLLME-GF AAS methodology was applied to the determination of cadmium in several water samples. Tap, sea and rivers water were collected from the North of Iran and were analyzed by DLLME combined with GF AAS for determination of cadmium. The concentration of cadmium in the tap, sea and rivers water samples were determined to be 15.2 ± 0.5, 6.8 ± 0.4, 7.0 ± 0.4 and 0.0 ng L^{-1} (not detected), respectively (Table-4). Tap, sea and rain water samples were spiked with cadmium standards to assess matrix effects. The relative recoveries of cadmium from tap, sea and rivers water at spiking level of 5 and 10 ng L^{-1} were 98, 94, 96 and 93 %, respectively (Table-4). These results demonstrated that the tap, sea and riverswater samples matrices, in present context, had little effect on DLLME of cadmium.

Comparison to other methods: A comparison of the represented method with other reported preconcentration methods is given in Table-5. In comparison with other reported methods, DLLME has low limit of detection (0.6 ng L^{-1}), high enrichment factor (118), short extraction procedure (less than 4 min) and low sample consumption (5 mL). These characteristics are of key interest for routine laboratories in trace metal ion analysis.

Conclusion

Dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry allows tackling the determination of cadmium in natural waters in a simple way. The method is simple, rapid and inexpensive. High preconcentration factor was obtained easily through this method and a detection limit at sub ng L^{-1} level was achieved with only 5.00 mL of sample. In this method sample preparation time as well as consumption of toxic organic solvents was minimized without affecting the sensitivity of the method. Although the obtained results in this work are related to

TABLE-4
DETERMINATION OF Cd(II) IN TAP, SEA AND RIVERS WATER SAMPLES AND RELATIVE RECOVERY OF SPIKED CADMIUM IN TAP, SEA AND RIVERS WATER SAMPLES

Relative recovery (%)	Found Cd^{2+} mean ± SD[a] (ng L^{-1})	Added Cd^{2+}	Concentration of Cd^{2+} mean ± SD[a] (ng L^{-1})	Sample
98	20.6 ± 0.5	5.0	15.2 ± 0.5	Tap water1[b]
94	11.5 ± 0.4	5.0	6.8 ± 0.4	Sea water[c]
96	11.3 ± 0.3	5.0	7.0 ± 0.4	Rain water [d]
93	9.8 ± 0.3	10.0	n.d.[f]	Tap water 2[e]

[a]Standard deviation (n = 3). [b]From drinking water system of Tehran, Iran. [c]Caspian sea water, Iran. [d]Rain water (Tehran, 26 January, 2006). [e]Tap water (Varamin, taken after 10 min operation of the tap). [f]Not detected.

TABLE-5
CHARACTERISTIC PERFORMANCE DATA OBTAINED BY USING DLLME AND OTHER TECHNIQUES IN DETERMINATION OF CADMIUM IN WATER

References	Calibration range (ng L^{-1})	Time (min)	Sample consumption (mL)	Enrichment factor	RSD[b] (%)	LOD[a] (ng L^{-1})	Method
[8]	6-300	2	14	24.6	3.2	2.8	On-line solvent extraction-GF AAS
[9]	100-4000	> 30	100	100	3.2	2.9	Co-precipitation-GF AAS
[20]	20-200	4	3	59.4	1.3	1.3	On-line SPE-GF AAS
[26]	0-20.0	> 30	10	50	2.1	5.9	CPE-GF AAS
[29]	10-1000	> 10	5	65	7.4	0.7	SDME-GF AAS
[Represented method]	2-21	< 4	5	118	3.4	0.6	DLLME-GF AAS

[a]Limit of detection. [b]Relative standard deviation.

cadmium determination, the system could be readily applied to the determination of other metals using various ligands, extractable by other organic solvents. Additional work is in progress on evaluating the performance of proposed method for the determination of other trace metal ions with spectrometric instruments.

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