

Liquid phase microextraction and ultratrace determination of cadmium by modified graphite furnace atomic absorption spectrometry

Saeid Nazari*

Department of Chemistry, Faculty of Science, Tarbiat Moallem University of Sabzevar, Sabzevar, Iran

ARTICLE INFO

Article history:

Received 20 April 2008

Received in revised form 25 August 2008

Accepted 25 September 2008

Available online 2 October 2008

Keywords:

Liquid phase microextraction

Preconcentration

Graphite furnace atomic absorption spectrometry

Cadmium

ABSTRACT

A powerful microextraction technique was used for determination of cadmium in water samples using liquid phase microextraction (LPME) followed by graphite furnace atomic absorption spectrometry (GF-AAS). In a preconcentration step, cadmium was extracted from a 2 ml of its aqueous sample in the pH 7 as 5,7-dibromoquinoline-8-ol (DBQ) complex into a 4 μ l drop of benzyl alcohol. After extraction, the micro drop was retracted and directly transferred into a graphite tube modified by [W.Rh.Pd](c). Some effective parameters on extraction and complex formation, such as type and volume of organic solvent, pH, concentration of chelating agent, extraction time and stirring rate were optimized. Under the optimum conditions, the enrichment factor and recovery were 450% and 90%, respectively. The calibration graph was linear in the range of 0.008–1 μ g L⁻¹ with correlation coefficient of 0.9961 under the optimum conditions of the recommended procedure. The detection limit based on the 3S_b criterion was 0.0035 μ g L⁻¹ and relative standard deviation (RSD) for eight replicate measurement of 0.1 μ g L⁻¹ and 0.4 μ g L⁻¹ cadmium was 5.2% and 4.5%, respectively. The characteristic concentration was 0.0032 μ g L⁻¹ equivalent to a characteristic mass of 12.8 fg. In order to evaluate the accuracy and recovery of the presented method the procedure was applied to the analysis of reference materials and seawater.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In spite of the high toxicity [1] of cadmium this element is widely used in industry, specially in electroplating, pigments for paints, enamel, glass, plastics, printing inks, rubber and lacquers, alloys, in the production of Ni–Cd batteries, as stabilizer in thermoplastics, for photoconductors and photoelectric solar cells, automobile tires and control rods in nuclear reactors. Food and cigarette smoke are the main sources of cadmium exposure for the general population. There are indications that the occurrence of this metal in foodstuffs has increased as a result of contamination of the environment [2]. Occupational exposure to cadmium occurs by inhalation and ingestion of fumes and dust of CdO and other Cd compounds and represents a significant hazard in industry. Workers are exposed to concentrations of cadmium that lead to a significant accumulation in the lungs, liver and kidneys [3]. Various organs might be affected after a long-term exposure to cadmium, e.g., kidney, lung and bone. It has also been suggested that cadmium is carcinogenic for humans and plays a role in the development of cardiovascular diseases, in particular, hypertension [2]. Exposure evaluation is monitored by using blood and urine as bio-

logical markers for recent exposure and body burden, respectively [4].

A variety of techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [5], ICP-atomic spectrometry [6,7], neutron activation analysis (NAA) [8], electrothermal atomic absorption spectrometry [9] and flame atomic absorption spectrometry (FAAS) [10] has been widely used for the determination of trace metal in different samples.

Although the development of modern analytical instruments allows 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 steps involved often employ large volumes of hazardous organic solvents, are time consuming and/or expensive. Besides, there might also be the problem of contamination and sample loss. As a consequence, different preconcentration techniques such as coprecipitation [11], solvent extraction [12] and solid phase extraction [13,14] have been used for analyte sample enrichment. Various solid materials such as ion exchange [15], chelating ion exchange resins [16], activated carbon [17], chitin [18], cellulose [19], naphthalene [20] and immobilized microorganisms on silica or sepiolite [21] have been used for preconcentration of trace metals. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent and by allowing sample extraction and

* Tel.: +98 571 4410104x3248; fax: +98 571 4410300.

E-mail address: nazari@sttu.ac.ir.

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 [22,23]. This technique uses simple equipment which is found in most analytical laboratories and also has been used for sample preparation of organic components and has coupled with chromatography methods. We developed this technique in our laboratory and reported for the first time on the coupling of liquid phase microextraction (LPME) with spectrometry to determine inorganic compounds. Using this technique, arsenic in variety of samples was determined [22].

In this paper we describe a new and extremely high sensitive method for extraction and determination of cadmium in aqueous samples by liquid phase microextraction combined with a graphite furnace atomic absorption spectrometry (LPME-GF-AAS). The results indicate that the LPME is an efficient extraction technique for analyzing cadmium in real samples, with very high pre-concentration factor, greatly increased sensitivity and low detection limit. The method is very simple and quick so that the overall time of extraction and determination for each sample is 10 min.

2. Experimental

2.1. Instrumentation

A Shimadzu model AA-6300G atomic absorption spectrometer (Kyoto, Japan) with GFA-EX7i graphite furnace atomizer and D2 lamp for background correction was used. A cadmium hollow cathode lamp (Hamamatsu photonics, Kyoto, Japan) was used as the radiation source adjusted at the operating current at the wavelength of 228.8 nm, lamp current 4 mA, spectral bandpass 0.5 nm and deuterium background correction. All measurements were performed using peak height and gas stop mode. The temperature program used to determine Cd by GFAAS is shown in Table 1.

All pH measurements were made by a Metrohm digital pH meter (model: 691, Herisua, Switzerland) with a combined glass electrode.

A 10 μ l Hamilton 7105 syringe (Hamilton, Reno, NV, USA) was used to suspend the drop of the acceptor phase and to inject it into the graphite furnace atomizer. Samples were stirred in 15 ml flat-bottom vials containing Teflon-line septa using an electronic magnetic stirrer (VWR Scientific, West Chester, PA, USA).

2.2. Reagents

All chemicals used were of analytical grade doubled distilled, dionized water was used throughout. A stock solution of 1000 μ g ml⁻¹ cadmium was prepared by dissolving 0.2744 g of Cd(NO₃)₂·4H₂O (Merck, Darmstadt, Germany) in 0.5 mol L⁻¹ nitric acid and diluting to 100 ml in a volumetric flask. More diluting solutions were prepared daily from the stock solution. The extraction organic phase was benzyl alcohol (Merck, Darmstadt, Germany). 1.0% (w/v) 5,7-dibromoquinoline-8-ol (DBQ) (Aldrich,

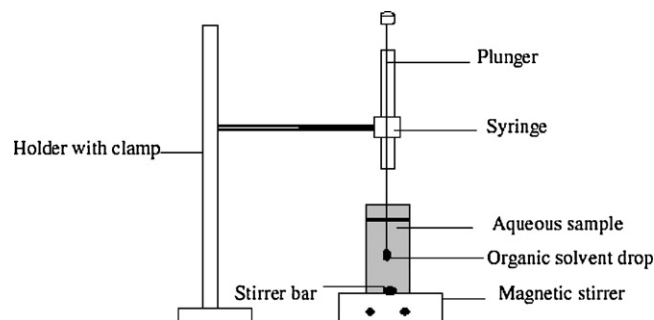


Fig. 1. The schematic setup for liquid phase microextraction.

USA) in ethanol was used as a complexing agent. Modifiers of 0.1% (w/v) Pd and Rh in HCl 2% (v/v), 0.1% (w/v) W, 10% (w/v) Ni in water were used.

2.3. Extraction procedure

Two ml of cadmium solution was adjusted at pH 7 and treated with 0.5 ml of 0.3% (w/v) 5,7-dibromoquinoline-8-ol was transferred to a 15 ml vial. Cadmium formed complex with 5,7-dibromoquinoline-8-ol. The solution was stirred by magnetic stirrer with a 6 mm stir bar at optimized speed 600 rpm. A 4 μ l of benzyl alcohol was taken by the Hamilton syringe and its needle was used to pierce the vial septum. The syringe was clamped in such a way that the tip of the needle was located at a fixed position in the sample solution as shown in Fig. 1. The syringe plunger was depressed to expose the drop and the stirring commenced. The Cd-5,7-dibromoquinoline-8-ol complex was extracted from aqueous solution into the benzyl alcohol as extraction organic phase.

After the extraction, the microdrop was retracted and directly injected into the graphite furnace tube modified with [Pd(c) + Pd(i)] for subsequent determinations. The different parameters affecting the technique such as solvent, pH, stirring rate, concentration of 5,7-dibromoquinoline-8-ol and time of extraction were optimized.

2.4. Tube modification

Ni modifier was used by injecting 0.2% (w/v) Ni and sample solution with equal volumes. [(W,Rh)(c) + Rh(i)] modifiers were used for coating containing 60 μ g of each of W and Rh from 0.1% (w/v) of their solutions at temperatures of 2200 °C and 2000 °C, respectively and injecting 10 μ l of 0.1% (w/v) Rh on top of 10 μ l sample solution (without extraction). [Pd(c) + Pd(i)] modifier was used as coating of 60 μ g Pd onto the graphite tube at 1800 °C and injecting of 10 μ l solution of 0.1% (w/v) Pd on top of 10 μ l of sample solution. [W,Rh,Pd](c) modifier was used as coating of 60 μ g of each of W, Rh and Pd solution at the appropriate temperatures. Added of 5,7-dibromoquinoline-8-ol to cadmium solution in direct injection without preconcentration step has not any effect on the signal.

3. Result and discussion

In order to obtain a high enrichment factor, the effect of different parameters affecting the complex formation and extraction conditions such as type and volume of organic solvent, pH, concentration of chelating agent, extraction time and stirring rate were optimized. One variable at a time optimization was used to obtain optimum conditions for liquid phase microextraction procedure.

Enrichment factor is defined as the ratio of concentration of cadmium in the microdrop phase to concentration of cadmium in the aqueous sample. Concentration of cadmium in the microdrop phase

Table 1
Temperature program for the determination of Cd using LPME-GFAAS.

Stage	Furnace temperature (°C)	Mode	Time (s)	Ar flow rate (L min ⁻¹)
Drying	150	Ramp	15	1.5
Ashing	300	Step	15	1.5
Atomization	1800	Step	3	Gas stop
Clean up	2500	Step	2	1.5

Table 2
Analytical figures of merit for cadmium determination using different chemical modifiers.

Chemical modifier	Detection ^a limit ($\mu\text{g L}^{-1}$)	Sensitivity ^b ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g L}^{-1}$)	RSD % ^c
Ni(i)	0.20	0.051	0.33–42	5.7
[(W.Rh)(c) + h(i)]	0.15	0.045	0.26–27	9.0
[Pd(c) + Pd(i)]	0.09	0.026	0.24–31	4.5
[W.Rh.Pd](c)	0.08	0.024	0.2–25	4.0

^a Based on 3Sb.

^b Calculated by dividing 0.0044 to the slope of calibration curve.

^c For 10 replicated analysis of 100 ng/ml cadmium.

was calculated from the calibration graph obtained by direct injection of cadmium into the modified graphite furnace tube without any preconcentration (by compare absorbance of direct injection and after preconcentration). Addition of complexing agent to the cadmium solution in direct injection without preconcentration step has not any effect on the signal.

3.1. Effect of type of modifiers

Several modifiers containing Pd, Ru, Rh, Ir, V, Mo, W, Ni, Mg, Ascorbic acid separately or in their combinations were tested. The results of best performing modifiers are shown in Table 2. [W.Rh.Pd](c) modifier showed the best results in contrast to [Pd(c) + Pd(i)] for direct determination of cadmium. Also [Pd(c) + Pd(i)] modifier showed the best results in determination of organic compounds of cadmium than [W.Rh.Pd](c) modifier.

3.2. Effect of type and volume of the extraction solvent

Effect of five different solvents, carbon tetrachloride, dichloromethane, 1,2 dichloroethane, nitrobenzene and benzyl alcohol was evaluated for the of 2 ml cadmium solution with concentration of $0.1 \mu\text{g L}^{-1}$. The results are given in Fig. 2. Benzyl alcohol was found to provide higher extraction efficiency. This may be attributed to greater polarity of benzyl alcohol than the others, which leads to the higher solubility of the polar Cd-5,7-dibromoquinoline-8-ol complex and hence higher extraction efficiency.

The influence of drop size was investigated in the range of 1–4 μl . It was found that the absorbance increases with drop volume in the range of 1–4 μl . When drop size exceeded 4 μl , it became too unstable to be suspended at the needle tip. For this reason 4 μl drop volume was used for further studies.

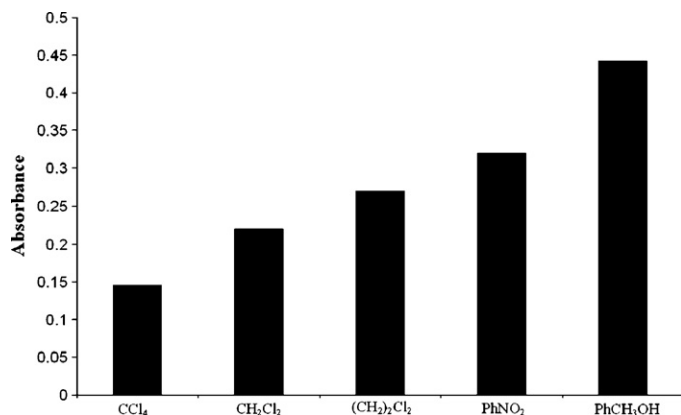


Fig. 2. Effect of type of extraction solvent on the absorbance obtained from LPME.

3.3. Effect of extraction time

Extraction time is one of the most important factors in the most of extraction procedures. The dependence of extraction efficiency upon extraction time was studied within a range of 0–30 min in the constant experimental conditions. Because the mass transfer is a time dependent process, the reaction time for the transfer Cd-5,7-dibromoquinoline-8-ol complex from solution into benzyl alcohol investigated. All measurements were carried out with $0.1 \mu\text{g L}^{-1}$ cadmium. Fig. 3 shows the absorbance of cadmium versus extraction time. The results showed an increase of the cadmium absorbance up to 10 min and leveling off at higher extraction time. Therefore 10 min was used as the optimum extraction time.

3.4. Effect of pH

The effect of pH on the complex formation and extraction of cadmium from water samples was studied within the range of 3.0–9.0. The results illustrated in Fig. 4 show that the absorbance is nearly constant in the range of 6.0–7.5. In order to obtain high extraction efficiency and minimize diverse ions interferences, pH 7 was chosen.

3.5. Effect of 5,7-dibromoquinoline-8-ol (DBQ) concentration

The influence of the concentration of 5,7-dibromoquinoline-8-ol in the aqueous solution on the cadmium cationic complex

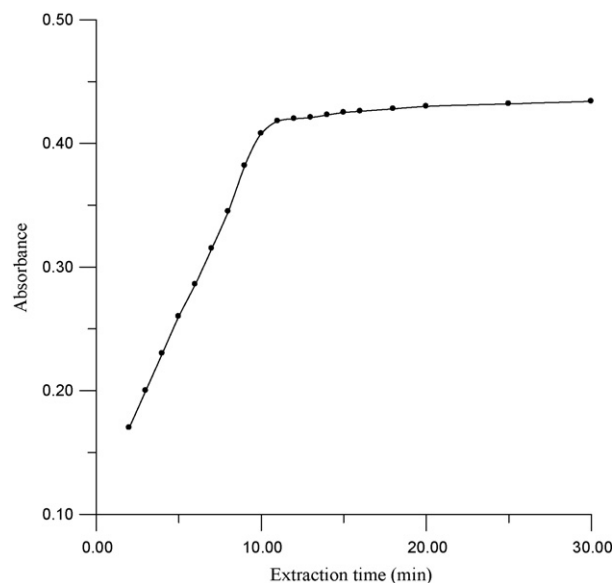


Fig. 3. Effect of extraction time on the absorbance of cadmium obtained from LPME.

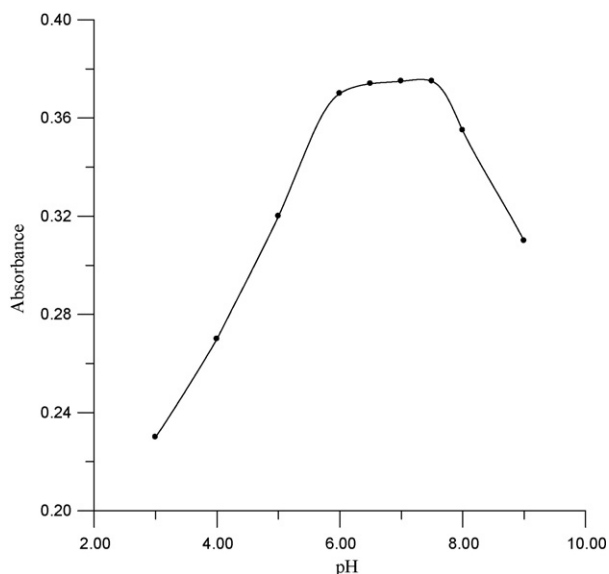


Fig. 4. Effect of pH on the absorbance of cadmium obtained from LPME.

formation was investigated for $0.1 \mu\text{g L}^{-1}$ solution of cadmium extracted for 10 min. Different concentrations (0.0–0.5%, w/v) of 5,7-dibromoquinoline-8-ol were used in the aqueous solution and its effects on the extraction process are shown in Fig. 5. As can be seen, the efficiency of cadmium transport increases with increasing 5,7-dibromoquinoline-8-ol concentration until 0.3% (w/v) is reached. However, a further increase in the concentration of 5,7-dibromoquinoline-8-ol (up to 0.4%) caused a pronounced decrease in the formation of cadmium complex. This is most probably due to the competition of 5,7-dibromoquinoline-8-ol itself with Cadmium-5,7-dibromoquinoline-8-ol complex for transfer through the LPME. Hence, 0.3% (w/v) was employed as the optimum concentration of 5,7-dibromoquinoline-8-ol.

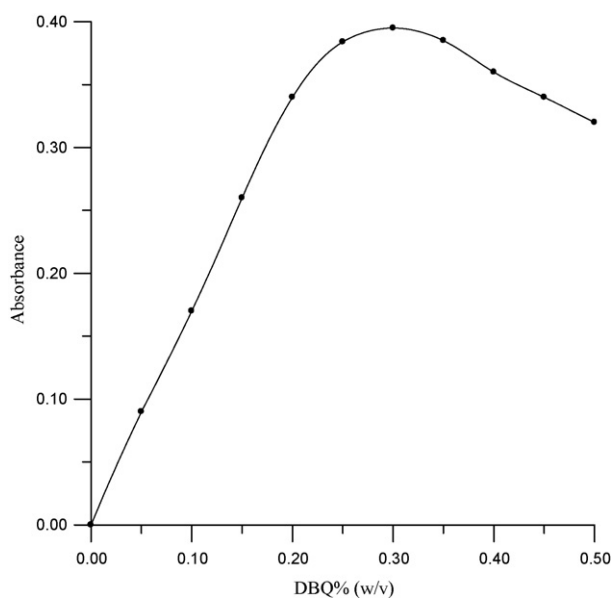


Fig. 5. Effect of concentration of 5,7-dibromoquinoline-8-ol on the absorbance of cadmium obtained from LPME.

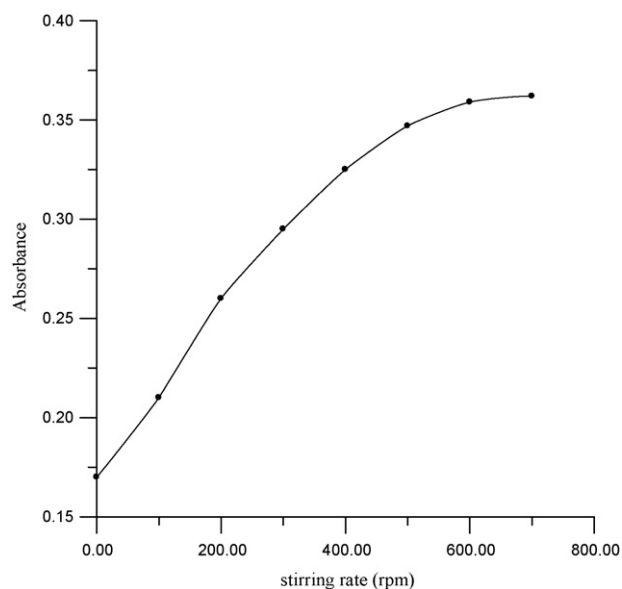


Fig. 6. Effect of stirring rate on the absorbance of cadmium obtained from LPME.

Table 3

Effect of foreign ions on determination of cadmium.

Foreign ions	Maximum tolerance ratio
Na ⁺ , Co ²⁺ , Li ⁺ , Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Ca ²⁺ , Zn ²⁺ , Fe ²⁺ ^a , Fe ³⁺ ^a , NH ₄ ⁺ , Ba ²⁺ , K ⁺ , Hg ²⁺ , Mg ²⁺ , WO ₄ ²⁻ , Br ⁻ , CH ₃ COO ⁻ , S ₂ O ₈ ²⁻ , MoO ₄ ²⁻ , PO ₄ ³⁻ , Cl ⁻ , CO ₃ ²⁻ , NO ₂ ⁻ , SeO ₃ ²⁻ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , SCN ⁻	1000
Cu ²⁺ , Cr ³⁺ , Sn ²⁺ , Al ³⁺	500

^a Masked with F⁻.

3.6. Effect of stirring rate

Magnetic stirring was used to facilitate the mass transfer process and thus improving the extraction efficiency. The stirring rate was optimized for extraction process. Fig. 6 illustrates the effects of stirring rate on the enrichment factor increased with increasing of the stirring rate up to 600 rpm, because in high stirring rate a relatively large vortex is formed in the lower region of the organic solvent, but instability of droplet limited the phenomenon, thus 600 rpm was chosen for further experiment.

3.7. Effect of interferences

The effect of various ions on the determination of $0.1 \mu\text{g L}^{-1}$ cadmium was investigated. A given species was considered to interfere if it resulted in a $\pm 5\%$ variation of the AAS signal. The results

Table 4

Analytical characteristics of LPME-GF AAS for determination of cadmium.

Parameter	Analytical feature
Linear range ($\mu\text{g L}^{-1}$)	0.008–1
Correlation coefficient	0.9961
Limit of detection ($\mu\text{g L}^{-1}$)	0.0035
Repeatability (RSD%) ($n=8$)	5.2% ^a , 4.5% ^b
Enrichment factor (EF) ^c	450
Recovery%	90
Sample volume (ml)	2

^a cadmium concentration was $0.1 \mu\text{g L}^{-1}$ for which RSD was obtained.

^b cadmium concentration was $0.4 \mu\text{g L}^{-1}$ for which RSD was obtained.

^c Enrichment factor is the slope ratio of calibration graph after and before extraction.

Table 5
Results (mean \pm standard deviation based on eight replicate analysis) of determination of cadmium in reference materials, water samples.

Sample	Cadmium added ($\mu\text{g L}^{-1}$)	Cadmium found ($\mu\text{g L}^{-1}$)	Recovery (%)
Sea water ^a	0	3.7 \pm 0.1	-
0.2	3.89 \pm 0.2	97	
0.3	4.00 \pm 0.2	99	
0.4	4.11 \pm 0.2	103	
Tap water	0	0.00	
0.2	0.198 \pm 0.01	99	
0.4	0.408 \pm 0.02	102	
Reference material	Certified value	Measured value	Recovery %
JB-1 ^a	0.11 ($\mu\text{g g}^{-1}$)	0.108 \pm 0.005 ($\mu\text{g g}^{-1}$)	98.2
JB-1a ^a	0.1 ($\mu\text{g g}^{-1}$)	0.099 \pm 0.004 ($\mu\text{g g}^{-1}$)	99.0
JB-2 ^a	0.14 ($\mu\text{g g}^{-1}$)	0.136 \pm 0.006 ($\mu\text{g g}^{-1}$)	97.1
NIST 2670 ^b	0.088 \pm 0.003 (mg L^{-1})	0.0894 \pm 0.004 ($\mu\text{g L}^{-1}$)	101.6

^a Collected from Caspian Sea.

^a Obtained from geological survey of Japan, GSJ.

^b From National Institute of Standard and Technology NIST (USA).

obtained are presented in Table 3. As can be seen the effect of various ions are negligible and cadmium can be determined quantitatively in real samples without interference from matrix of the samples. Maximum tolerance ratio is the maximum ratio of foreign ion to Cd to that ratio foreign ions have not any interference in determination of Cd. For Cu^{2+} , Cr^{3+} , Sn^{2+} and Al^{3+} maximum tolerance ratio is less than another ions (500) because these ions could probably formed complex with 5,7-dibromoquinoline-8-ol in the aqueous solution.

3.8. Analytical figure of merits

Analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility and enhancement factor are listed in Table 4. The calibration the optimum conditions of the recommended procedure. The regression equation is $A = 0.0026 (\pm 0.00051) + 0.56C (\pm 0.0099)$, where A is the absorbance and C the concentration of cadmium in $\mu\text{g L}^{-1}$ in the initial solution. The calibration graph was linear in the range of 0.008–1 $\mu\text{g L}^{-1}$ with correlation coefficient of 0.9961 under the optimum conditions of the recommended procedure. The detection limit was calculated as three times the standard deviation of the peak absorbance for injection of 4 μl of eight extractions of the blank, using the liquid phase microextraction procedure. The detection limit was calculated to be 0.0035 $\mu\text{g L}^{-1}$ with absolute value of 14 fg for 4 μl injection into the graphite furnace. The characteristic concentration was 0.0032 $\mu\text{g L}^{-1}$ equivalent to a characteristic mass of 12.8 fg. The relative standard deviation (RSD) for eight replicate measurement of 0.1 $\mu\text{g L}^{-1}$ and 0.4 $\mu\text{g L}^{-1}$ cadmium was 5.2% and 4.5%, respectively. The enrichment factor (EF) was obtained from the slope ratio of calibration graph after and before extraction, which was about 450. The extraction recovery ($R\%$) was 90% which was calculated by Eq. (1).

$$R\% = \left(\frac{V_{\text{drop}}}{V_{\text{solution}}} \right) \times \text{EF} \times 100 \quad (1)$$

3.9. Application

In order to evaluate the accuracy and recovery of the proposed method, standard reference materials SRM 2670 (freeze-dried urine) from NIST (USA), JB-1, JB-1a and JB-2 as powder obtained from geological survey of Japan (GSJ) were analysed for their cadmium contents. The powder was dissolved in 15 ml of a mixture of 500 ml HF, 165 ml H_2SO_4 and 40 ml HNO_3 at 150 $^\circ\text{C}$ in a teflon beaker overnight. To show the applicability of the method,

seawater from Caspian Sea and local tap water was analysed for its cadmium content. The results obtained are presented in Table 5.

4. Conclusions

The results of the presented investigation show that liquid phase microextraction combined with [W.Rh.Pd](c) modified tube graphite furnace atomic absorption spectrometry is a powerful technique for the preconcentration and determination of low levels of cadmium for analysis in variety of samples. Good preconcentration was obtained easily through this method and low detection limit was achieved with only 2 ml of sample. The method is also simple, inexpensive and reproducible and applied for sea and tap water samples. The method also can be applied for analysis of real samples such as biological and botanical samples.

References

- [1] D.L. Tsalev, Z.K. Zaprianov, Atomic Absorption Spectrometry in Occupational and Environmental Health Practice, 2nd ed., vol.1, CRC Press, USA, 1985, p. 105.
- [2] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Cadmium, U.S. Department of Health and Human Services, Public Health Service, U.S. Government Printing Office, USA, 1998.
- [3] L.A. Saryan, C. Zenz, Cadmium, in: O.C. Zenz, B. Dickerson, E.P. Horvath (Eds.), Occupational Medicine, 3rd ed., Mosby-Year Book, Inc., USA, 1994, p. 481.
- [4] C.G. Elinder, L. Friberg, T. Kjellström, G. Nordberg, G. Oberdoerster, Biological Monitoring of Metals, World Health Organization, Switzerland, 1994.
- [5] J. Wank, E.H. Hansen, Coupling sequential injection on-line preconcentration using a PTFE beads packed column to direct injection nebulization inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom 17 (10) (2002) 1278–1283.
- [6] S.J. Hill, J. Hartley, L. Ebdon, Determination of trace metals in volatile organic solvents using inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom 7 (1992) 23–28.
- [7] M.A. Hamilton, P.W. Rode, M.E. Merchant, J. Sneddon, Determination and comparison of heavy metals in selected seafood, water, vegetation and sediments by inductively coupled plasma-optical emission spectrometry from an industrialized and pristine waterway in Southwest Louisiana, Microchem. J. 88 (2008) 52–55.
- [8] N. Lavi, Z.B. Afassi, Determination of trace amounts of cadmium, cobalt, chromium, iron, molybdenum, nickel, selenium, titanium, vanadium and zinc in blood and milk by neutron activation analysis, Analyst 115 (1990) 817–822.
- [9] E.I. Verda, L. Palomo Gil, T.S. Cordero, A. Garcia Torres, J.M. Cano Pavon, Automatic on-line column preconcentration system for determination of cadmium by electrothermal atomic absorption spectrometry, J. Anal. At. Spectrom 16 (2001) 293–295.
- [10] L. Narin, M. Soyulak, L. Elici, M. Dogan, Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column, Talanta 52 (6) (2000) 1041–1046.
- [11] D. Atanasova, V. Stefanova, E. Russeva, Co-precipitative pre-concentration with sodium diethyldithiocarbamate and ICP-AES determination of Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr and Cd in water, Talanta 47 (5) (1998) 1237–1243.

- [12] L. Kojima, M. Katsuzaki, Selective extraction and "One-Drop" flame atomic absorption spectrometric determination of silver in biological standard reference materials, *Anal. Sci* 13 (1997) 1021–1023.
- [13] M.E. Mahmoud, M.M. Osman, M.E. Amer, Selective pre-concentration and solid phase extraction of mercury(II) from natural water by silica gel-loaded dithione phases, *Anal. Chem. Acta* 415 (1–2) (2000) 33–40.
- [14] Y.P. Depena, M. Gallego, M. Valcarcel, On-line sorbent extraction, preconcentration and determination of lead by atomic absorption spectrometry, *Talanta* 42 (2) (1995) 211–213.
- [15] A. Tunceli, A. Rehber Toker, Flame atomic absorption spectrometric determination of silver after preconcentration on Amberlite XAD-16 resin from thiocyanate solution, *Talanta* 51 (5) (2000) 889–894.
- [16] M.C. Yebra, J. Salgado, L. Puig, A. Moreno-cid, Field preconcentration of cadmium from seawater by using a minicolumn packed with Amberlite XAD-4/4-(2-pyridylazo) resorcinol and its flow-injection-flame atomic absorption spectrometric determination at the ng L^{-1} Level, *Anal. Bioanal. Chem* 374 (2002) 530–534.
- [17] S. Cerutti, M.F. Silva, J.A. Gasquez, R.A. Olsina, L.D. Martinez, On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, *Spectrochim. Acta B* 58 (1) (2003) 43–50.
- [18] S. Hoshi, K. Konuma, K. Sugawara, M. Uto, K. Akatsuka, The simple and rapid spectrophotometric determination of trace chromium(VI) after preconcentration as its colored complex on chitin, *Talanta* 47 (3) (1998) 659–663.
- [19] K. Zih-perenyi, A. Lasztity, Zs. Horvath, A. Levai, Use of a new type of 8-hydroxyquinoline-5-sulphonic acid cellulose (sulphoxine cellulose) for the preconcentration of trace metals from highly mineralised water prior their GFAAS determination, *Talanta* 47 (1998) 673–679.
- [20] N. Pourreza, M. Behpour, Column preconcentration of aluminum using eriochrome cyanine R and methyltrioctylammonium chloride adsorbent supported on naphthalene with subsequent spectrophotometric determination, *Microchem. J* 63 (2) (1999) 250–256.
- [21] H. Bag, A. Rehber Toker, M. Lale, Determination of Cu, Zn, Fe, Ni and Cd by flame atomic absorption spectrophotometry after preconcentration by *Escherichia coli* immobilized on sepiolite, *Talanta* 51 (5) (2000) 1035–1043.
- [22] M. Chamsaz, M.H. Arbab-Zavar, S. Nazari, Determination of arsenic by electrothermal atomic absorption spectrometry using headspace liquid phase microextraction after *in situ* hydride generation, *J. Anal. At. Spectrom* 18 (2003) 1279–1282.
- [23] M. Kaykhaii, S. Nazari, M. Chamsaz, Determination of aliphatic amines in water by gas chromatography using headspace solvent microextraction, *Talanta* 65 (2005) 223–228.