



Solidified floating organic drop microextraction for pre-concentration and trace monitoring of cadmium ions in environmental food and water samples

Ahmad Alahabadi¹ · Ayoob Rastegar^{1,3} · Ali Esrafil^{2,3} · Zahra Rezai¹ · Ahmad Hosseini Bandegharai^{1,4} · Mahdi Farzadkia^{2,3}

Received: 29 December 2016 / Accepted: 29 March 2017 / Published online: 7 April 2017
© Iranian Chemical Society 2017

Abstract In this research, solidified floating organic drop microextraction as an efficient sample preparation method was used for trace monitoring of cadmium ions in environmental samples. In this method, a free microdroplet of 1-undecanol is floated on the surface of aqueous solution and agitated by a stirring bar placed on the bottom of the sample vial. Cadmium ions were complexed with neocuproine to obtain hydrophobic complex and extracted to extraction solvent. The extracted target ions were determined by flow injection–flame atomic absorption spectrometry. The effect of important factors on the extraction of target ions by the proposed sample preparation method was evaluated and optimized. The limit of detection, relative standard deviation (%) and enrichment factor of the method were 0.02, 3.7 and 98.5%, respectively. The validation of the method was examined by the analysis of cadmium ions in the certified reference material (sea food mix), and the obtained data can proof the reliability of the

method for trace detection of cadmium ions. The method was successfully applied for determination of cadmium in the real food and water samples, and satisfactory relative recoveries (97–102%) were achieved.

Keywords Solidified floating organic drop microextraction method · Flow injection · Neocuproine · Trace monitoring of cadmium · Food samples

Introduction

According to the toxicity of heavy metals for human health, the monitoring of heavy metals at trace levels in environmental samples is having more importance in recent years [1–3]. Cadmium is among 13 toxic metal species on the preference contamination list of the Environmental Protection Agency (EPA) [4]. Accurate analysis of trace amount metal ions is a complex analytical process. Analysis of trace metal ions present in various matrices such as natural and wastewater, sediment and tissue with some analytical techniques such as atomic absorption methods is not possible according to the matrix effect of potentially interfering ions and low concentration of metal ions in the sample, and therefore, for trace detection of heavy metals in real samples it is a necessity to pre-concentrate the target ions before their analysis to raise the concentration of the analyte ions to be determined [5–11]. Different liquid-phase microextraction methods (LPMEs) such as [12, 13] dispersive liquid–liquid microextraction (DLLME) [14–18], solid-phase extraction (SPE) [19–22] and cloud point extraction (CPE) [23–25] have been widely used in analytical chemistry.

Recently, an easy and impressive sample preparation method based on LPME was initially used for the

Electronic supplementary material The online version of this article (doi:10.1007/s13738-017-1113-1) contains supplementary material, which is available to authorized users.

✉ Ali Esrafil
a_esrafil@yahoo.com

- ¹ Department of Environmental Health Engineering, School of Public Health, Sabzevar University of Medical Sciences, Sabzevar, Iran
- ² Research Center for Environmental Health Technology, Iran University of Medical Sciences, Tehran, Iran
- ³ Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran
- ⁴ Department Engineering, Kashmar Branch, Islamic Azad University, P.O. Box 161, Kashmar, Iran

polycyclic aromatic hydrocarbons monitoring in water samples by Yamini et al. [26]. In this method, a free microdrop of the organic solvent (the melting point of the organic solvent should be near room temperature in the range of 10–30 °C) is placed to the surface of an aqueous sample, while being rotated by a stirring bar in the sample solution. Under the proper stirring conditions, the suspended microdrop can remain in the top-center position of the sample solution. After fulfillment of the extraction, the sample vial is cooled by placing it in an ice bath for 4 min. The solidified extraction solvent is then transferred into a conical vial, where it melts immediately. Finally, the analytes detection in the extractant can be performed by gas chromatography. This quantitative LPME method is a green and suitable analytical procedure, for which excellent validity and accuracy are illustrated, being simpler and more convenient, compared with the common sample preparation methods [27–33]. After one year of presentation of solidified floating organic drop microextraction (SFODME) technique for separation of organic substances, the feasibility of performance of SFODME in combinations with electrothermal atomic absorption spectrometry for trace monitoring of metal ions was considered and a SFODME method for ultra-trace monitoring of lead was evaluated [34]. The method was based on efficient extraction of lead into 20 μL of 1-undecanol containing dithizone as a chelating agent. In the next step, the extracted organic solvent was solidified and transferred into a conical vial where it melted promptly and was determined by graphite furnace atomic absorption spectrometry. An enrichment factor of 500 was obtained with 5-min extraction time. Dadfarnia et al. [35] reported for the first time trace detection of cadmium ions by SFODME according to the extraction of an ion pair into 1-undecanol and then analysis by flow injection–flame atomic absorption spectrometry.

In the present work, a simple, selective, sensitive and reliable sample preparation technique according to the SFODME was designed for pre-concentration and extraction of cadmium ions at trace levels in different environmental real samples. The main parameters impressing the extraction efficiency such as solution's pH, concentration of neocuproine, stirring rate, extraction time, solution's temperature and salt concentration on the extraction and determination of cadmium ions by the applied sample preparation method were considered and optimized. The developed method (SFODME) was applied for trace detection of cadmium ions in several food and water samples, and the accuracy of the proposed method was confirmed by standard reference material.

Experimental

Chemical and reagents

All analytical-grade reagents including solvents (the organic extractant was 1-undecanol) was purchased from Merck Company (Merck, Darmstadt, Germany). 2,9-Dimethyl-1,10-phenanthroline [neocuproine (high purity)] were obtained from Merck (Darmstadt, Germany). Milli-Q purification system (Millipore, Bedford, MA, USA) was used for the preparation of double-distilled water. Cd (II) stock solution (100 mg L^{-1}) was prepared by dissolution of the proper amount of $\text{Cd}(\text{NO}_3)_2$ (Merck, Darmstadt, Germany) in 3:1, HCl/HNO_3 (v/v) according to the standard methods and then diluted with double-distilled water. Adequate dilution of the stock standard solutions was applied for preparing of the working standard solutions step by step.

Apparatus

Concentration of cadmium ions was determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (FAAS) in an air–acetylene flame (air and acetylene flow rate 10 and 2.5 L min^{-1} , respectively), according to the user's manual provided by the manufacturer. A cadmium hollow cathode (lamp current 4.0 mA for cadmium) with the radiation of 228.8 nm was used as source. A variable flow-rate peristaltic pump was used to pump carrier streams and the sample through the manifold at a flow rate of 4.0 mL min^{-1} . Manifold lines consisted of 0.8 mm i.d. polyethylene tubing. The six-way injection valve allowed the sample to be directly loaded into a 50 μL loop and subsequently injected into the carrier stream. The pH was measured at $25 \pm 1 \text{ }^\circ\text{C}$ with a digital Metrohm ion analyzer (Herisau, Switzerland) equipped with a combined glass–calomel electrode. Hettich centrifuge model EBA 20 (Oxford, England) was employed for phase separation.

Sample pre-treatment for cadmium analysis in food and water samples

The analyzed food and agricultural products by the applied sample preparation method were shrimp, fish, lettuce, apple, mushroom, kiwi, Citrus limetta, pomegranate, wheat, tomato, potato, celery and olive. The mentioned agricultural products were purchased from the supermarket in Tehran (Iran). 1.0 g of dried and grounded samples was placed into burning cup with 15 mL of pure HNO_3 . The microwave (MARS 5) digestion conditions were used as; 6 min for 250 W, 6 min for 400 W, 6 min for 550 W,

6 min for 250 W, ventilation: 8 min. The resulted aqueous from digestion of food samples under the mentioned condition was separated by Whatman No. 42. After filtration of digested samples, the obtained clear solution was diluted to 10.0 mL (pH of 7.0) for cadmium analysis.

River (Siahrood River), sea (Caspian Sea) and tap (Tehran, Iran) water samples, used for evaluation of the proposed sample preparation method, were collected in PTFE tubes from the north region of Iran, and their pH were adjusted to 7.0 for further analysis.

Solidified floating organic drop microextraction procedure

An optimized concentration of the ligand was added into 10 mL of sample solution containing $10 \mu\text{g L}^{-1}$ of cadmium ions, and the resulted solution was stirred. Then, 30 μL of the 1-undecanol as an organic extraction solvent was placed on the surface of the sample solution by a microsyringe. The primary experimental results showed that 1-undecanol has the appropriate conditions for the extraction of the target analyte [36]. Therefore, 1-undecanol was selected as extraction organic solvent in the further experiments. As the sample solution flowed around the organic drop continuously, the formed complex between cadmium and neocuproine (ligand) was extracted into the extraction organic solvent. After a desired period of extraction, the cooling of extraction solvent was carried out by placing the sample vial in a refrigerator for 5 min. Then, the solidified solvent was transferred with a spatula into the conical vial and melted quickly at the room temperature. In the next step, the melted organic solvent was diluted to 100 μL with ethanol. Finally, 50 μL of the mentioned extracted target ions was detected by flow injection–flame atomic absorption technique.

Results and discussion

The performance of the proposed sample preparation method combined with FI-FAAS was examined for trace detection of cadmium ions in this work. Several factors which affect the extraction process comprise concentration of ligand, solution's pH, stirring rate, extraction time, the concentration of salt and solution's temperature were examined and optimized. In this experiment, 10.0 mL of double-distilled water spiked with $10 \mu\text{g L}^{-1}$ of cadmium ions was used to optimize the extraction factors under various experimental conditions. All the experiments were monitored in triplicate, and the mean of the results were used for optimization of parameters.

Effect of pH

In this work, the pH value plays an essential role in cadmium–neocuproine complex formation and subsequent extraction with organic extraction solvent (1-undecanol). Thus, the influence of pH of solution on the extraction efficiency of cadmium ions was evaluated in the pH range of 2.0–9.0. The other parameters were: volume of extraction solvent (1-undecanol), 30 μL ; concentration ratio of neocuproine to cadmium, 10; NaCl, 3% (w/v); stirring rate, 400 rpm; temperature, room temperature; extraction time, 15 min. According to the obtained data, the maximal signal for cadmium ions determination was obtained in the pH of 7.0. The interaction of cadmium ions with neocuproine increased from pH 2.0 to 7.0 but decreased from pH 7.0 to 9.0. By decreasing the pH of the solution, the extraction of target ions was also decreased due to electrostatic repulsion of the protonated active sites of ligand with the positively charged cadmium species. Meanwhile, the observed decrease in extraction of cadmium ions at the pH values higher than 7.0 is most probably due to the precipitation of target ions in the hydroxide form, which ends up to decrease in the concentration of free cadmium ions in the sample. Thus, pH of 7.0 was chosen as the optimum pH for further experiments.

Effect of amounts of neocuproine

The influence of the concentration ratio of ligand (neocuproine) to target ions [Cd(II)] on the extraction efficiency of cadmium ions was also investigated. According to the obtained data, the absorbance signal of Cd(II) increased with the increase in Cd(II)-to-neocuproine ratio of 1–10 (Fig. 1) and kept constant with subsequent increasing to the ratio of 15. According to the obtained data, the concentration ratio of 10 was used in the other experimental parameters.

Effect of salt addition

By increasing of ionic strength in the extraction solution, several effects can be occurred. The diffusion rate of the target analytes into the extraction solvent reduce by changing the Nernst diffusion film [28]. On the other hand, salting out effect led to an increase on the extraction efficiency of target ions [the cations and anions of the solvent (H_2O) interact with cations and anions of the salt (salting out effect)]. Therefore, in this condition the cadmium ions are free and can interact completely with applied ligand. Salt addition can be used to assist the completely extraction of target ions to organic solvent according to the salting out effect. To evaluate the influence of ionic strength

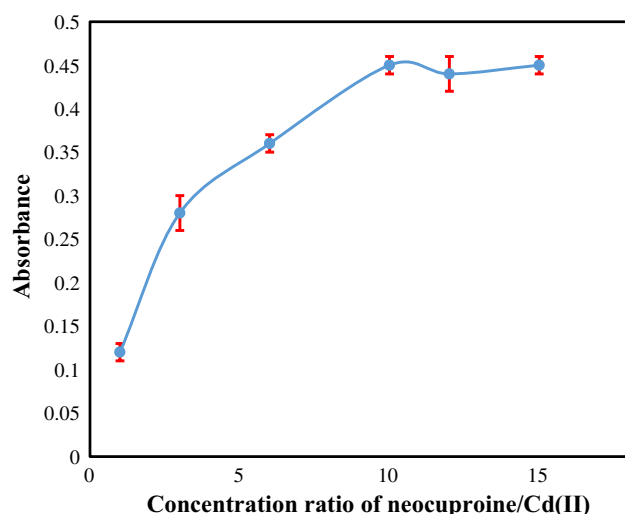


Fig. 1 Effect of amounts of neocuproine on the absorbance of Cd(II) by SFODME. Conditions: sample volume: 10 mL, volume of extraction solvent (1-undecanol), 30 μL ; Cd(II) concentration: 10 $\mu\text{g L}^{-1}$; pH of solution, 7.0; salt amounts, 3 (w/v %); stirring rate, 400 rpm; temperature, room temperature; extraction time, 15 min (number of replicate = 3)

on the efficiency of the applied sample preparation of cadmium ions, various experiments were applied by adding varying NaCl amounts from 0 to 5% (w/v) and other extraction parameters were constant. According to the absorbance signal for cadmium ions, with increasing of salt concentration in the range of 0–3% (w/v) the extraction yield gradually increases (Fig. 2). Thus, the next extraction experiments were carried out with a NaCl concentration of 3% (w/v).

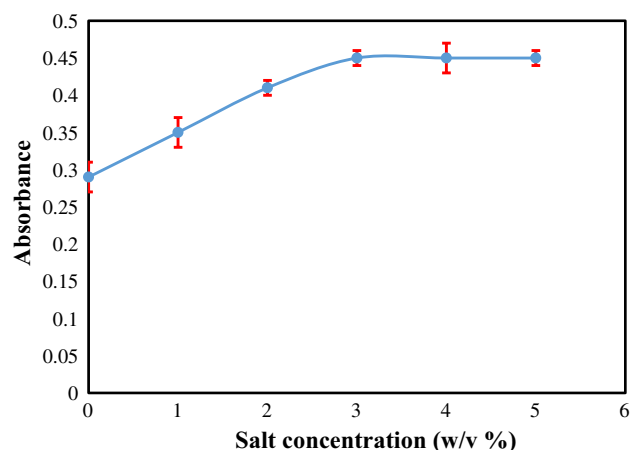


Fig. 2 Effect of salt addition on the absorbance of Cd(II) by SFODME. Conditions: sample volume: 10 mL, volume of extraction solvent (1-undecanol), 30 μL ; Cd(II) concentration: 10 $\mu\text{g L}^{-1}$; pH of solution, 7.0; concentration ratio of neocuproine to cadmium, 10; stirring rate, 400 rpm; temperature, room temperature; extraction time, 15 min (number of replicate = 3)

Effect of stirring rate

Sample stirring is another significant parameter having a great role in its capability to increase extraction efficiency and to decrease extraction time [34]. In the proposed sample preparation technique, the agitating speed has an important influence on both the form of the droplet and the mass transfer characteristic in the aqueous sample solution. The evaluation of the stirring rate on the extraction efficiency of cadmium ions was performed in the range of 0–1250 rpm. The obtained data are summarized in Figure 1S (ESM), and as can be seen from this figure, the analytical signal increased with increasing agitating rate from 0 to 400 rpm and then remained constant with further increase in a stirring rate up to 800 rpm. Higher stirring rates made a decrease in extraction, probably because of splashing and damaging of the droplet. Thus, 400 rpm was selected for the next extraction experiments.

Effect of temperature

The investigation of temperature effect on the extraction efficiency of target ion was carried out by varying the temperature between 25 and 60 $^{\circ}\text{C}$. The results are illustrated in Fig. 3. It was observed that the extraction yield is fixed in the temperature range of 25–40 $^{\circ}\text{C}$; but subsequent increase in temperature causes a decrease in analytical signal, which might according to the increase solubility of extraction solvent (organic phase) at higher temperatures or may be due to the decreasing of distribution ratio of cadmium–neocuproine complex at higher temperatures. Therefore, room temperature was used for further experiments.

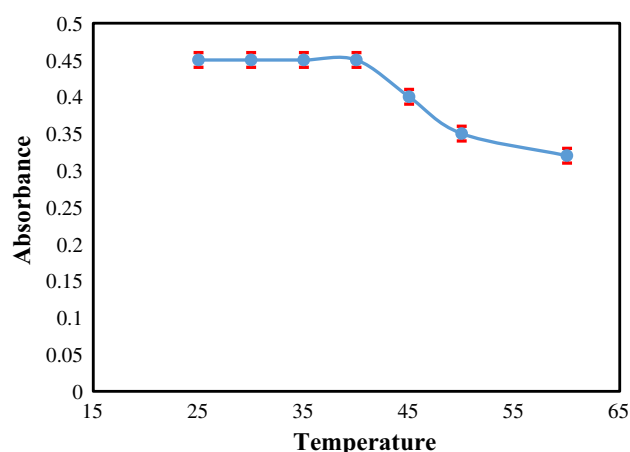


Fig. 3 Effect of temperature on the absorbance of Cd(II) by SFODME. Conditions: sample volume: 10 mL, volume of extraction solvent (1-undecanol), 30 μL ; Cd(II) concentration: 10 $\mu\text{g L}^{-1}$; pH of solution, 7.0; concentration ratio of neocuproine to cadmium, 10; salt amounts, 3 (w/v %); stirring rate, 400 rpm; extraction time, 15 min (number of replicate = 3)

Effect of extraction time

The extraction of target ions at a given time is affiliate on the mass transfer of cadmium ions from aqueous solution to the organic solvent drop. A period of time is required for equilibrium of this procedure. The dependence of extraction efficiency to extraction time was investigated within a range of 5–30 min under the constant experimental conditions. The results in Figure 2S (ESM) showed that with the increase in time up to 15 min, the absorbance increased and then remained fixed. So, 15 min was selected as the extraction time for the proposed sample preparation method.

The effect of the potentially interfering ions

To investigate the effect of potentially interfering ions, the potentially interfering ions that are present in food samples were added to 10 mL of solution including $10 \mu\text{g L}^{-1}$ of cadmium ions. The tolerance degree for analysis of cadmium ions in the presence of potentially interfering ions is summarized in Table 1S (ESM). According to the tolerance data, the potentially interfering ions have no significant effect on extraction and pre-concentration of cadmium ions by the proposed sample preparation method at optimum conditions.

Analytical performance

A calibration curve was sketched for the detection of cadmium ions according to the extraction procedure at optimum conditions. Linearity was obtained between 0.1 and $50 \mu\text{g L}^{-1}$ for cadmium ions in the aqueous solution. The correlation of determination (r^2) was 0.99. In the limits of

detection ($C_{\text{LOD}} = 3S_b/m$), S_b is the standard deviation of eight replication of blank signals and m is the tilt of the calibration curve after pre-concentration for a sample volume of 10 mL. The obtained LOD for the proposed sample preparation method was found to be $0.02 \mu\text{g L}^{-1}$. The relative standard deviation for 6 separate extraction experiments for the monitoring of 1 and $10 \mu\text{g L}^{-1}$ of target ions was 3.7 and 2.9%, respectively. The corresponding relative standard deviation (RSD), limit of detection (LOD), dynamic linear range (DLR), regression equation and correlation of determination (r^2) at optimized conditions are presented in Table 1. Furthermore, the enhancement factor calculated as the ratio between the slopes of the calibration curves acquired by the proposed method and through the direct analysis of cadmium standards by FAAS was found to be 97.5 ($38.26/0.388 = 98.5$).

Table 3 Comparison between measured values of cadmium ions by the proposed method and the certified values in sea food mix

Sample	Sea food mix
Element	Cadmium
Certified value (C_{CRM})	$4.76 \pm 0.03 \text{ mg g}^{-1}$
Laboratory measurement (C_m)	$4.64 \pm 0.04 \text{ mg g}^{-1}$
u_{CRM}	$0.03/2 = 0.015$
u_m	$0.04/5 = 0.008$
Δ_m	$ 4.76 - 4.64 = 0.12$
u_Δ	$\sqrt{0.015^2 + 0.008^2} = 0.017$
$U_\Delta = 2u_\Delta$	0.24
$U_\Delta \geq \Delta_m$	The measured mean value is not significantly different from the certified value

Table 1 Figure of merits of SFODME method for determination of cadmium ion

Method	Regression equation	r^2	DLR ($\mu\text{g L}^{-1}$)	RSD (%)	LOD ($\mu\text{g L}^{-1}$)
SFODME-FI-FAAS	$Y = 38.26C \text{ (mg L}^{-1}\text{)} + 0.0005$	0.99	0.1–50	3.7	0.02

Table 2 A comparison between the proposed sample preparation method and previously published articles for trace detection of cadmium ions

Method	LOQ ($\mu\text{g L}^{-1}$)	RSD (%)	ET ^a (min) or flow rate (mL min^{-1})	EF ^b ; sample volume (mL)	Refs.
Cd(II)-IIP	0.5	4.2	7	60; 150	[37]
MWCNT/P2AT	1.0	2.4	6 mL min^{-1}	100; 500	[38]
CPE ^c	6.0	2.1	25	23; 10	[39]
DLLME ^d	1.0	0.9	Fast	13; 40	[40]
SFODME	1.0	4.7	10	205; 100	[41]
SFODME	0.1	3.7	15	98.5; 10	This work

^a Extraction time (in the sample preparation method)

^b Enhancement factor

^c Cloud point extraction

^d Dispersive liquid–liquid microextraction

Table 4 Analysis of cadmium in different food (A) and water (B) samples

	Element	Real sample ($\mu\text{g kg}^{-1}$)	Added ($\mu\text{g kg}^{-1}$)	Founded ($\mu\text{g kg}^{-1}$)	RSD (%)		RR (%)
					Inter-day	Intra-day	
(A) Food sample							
Citrus limetta	Cadmium	3.5	5.0	8.4	3.8	4.1	98.0
			10.0	13.2	3.9	4.3	97.0
			20.0	23.1	4.1	4.5	98.0
Apple	Cadmium	4.2	5.0	9.1	4.2	5.1	98.0
			10.0	14.2	4.2	4.8	100.0
			20.0	24.3	3.5	4.3	100.5
Fish sample	Cadmium	7.8	5.0	12.9	4.3	4.5	102.0
			10.0	17.5	4.5	4.9	97.0
			20.0	27.3	3.8	4.4	97.5
Shrimp sample	Cadmium	8.4	5.0	13.2	4.4	4.9	96.0
			10.0	18.5	4.8	5.1	101.0
			20.0	28.1	4.2	4.9	98.5
Celery	Cadmium	1.9	5.0	7.1	4.6	4.8	104.0
			10.0	12.1	4.4	4.8	102.0
			20.0	22.1	4.6	5.1	101.0
Mushroom	Cadmium	Not detected	5.0	4.9	4.6	4.9	98.0
			10.0	9.9	5.1	5.2	99.0
			20.0	19.8	4.8	5.1	99.0
Lettuce	Cadmium	Not detected	5.0	5.1	4.9	4.9	102.0
			10.0	9.8	5.3	5.2	98.0
			20.0	19.6	4.6	5.1	98.0
Kiwi	Cadmium	1.7	5.0	6.6	3.9	4.7	98.0
			10.0	11.6	4.5	5.0	99.0
			20.0	21.5	4.0	4.3	99.0
Tomato	Cadmium	1.5	5.0	6.5	4.3	4.6	100.0
			10.0	11.7	5.1	4.7	102.0
			20.0	21.7	4.5	4.9	101.0
Wheat	Cadmium	Not detected	5.0	4.9	4.1	4.5	98.0
			10.0	9.9	3.9	4.7	99.0
			20.0	19.7	4.4	4.9	98.5
Olive	Cadmium	1.3	5.0	6.3	4.4	4.8	100.0
			10.0	11.5	4.3	4.5	102.0
			20.0	21.5	5.1	4.9	101.0
Potato	Cadmium	5.8	5.0	10.6	4.7	5.1	96.0
			10.0	15.5	4.5	4.9	97.0
			20.0	25.3	5.1	4.9	97.5
Pomegranate	Cadmium	2.8	5.0	7.7	4.9	4.7	98.0
			10.0	12.9	4.2	5.1	101.0
			20.0	22.5	4.8	5.5	98.5
(B) Water sample							
Tap water	Cadmium	–	5.0	4.9	4.1	5.1	98.0
			10.0	9.9	3.7	4.4	99.0
			20.0	19.7	3.2	4.8	98.5
River water	Cadmium	1.2	5.0	6.2	4.1	4.9	100.0
			10.0	11.4	3.5	4.5	101.8
			20.0	20.9	3.9	4.6	98.5

Table 4 continued

	Element	Real sample ($\mu\text{g kg}^{-1}$)	Added ($\mu\text{g kg}^{-1}$)	Founded ($\mu\text{g kg}^{-1}$)	RSD (%)		RR (%)
					Inter-day	Intra-day	
Seawater	Cadmium	1.8	5.0	6.9	3.1	4.2	102.0
			10.0	11.5	4.1	4.5	97.5
			20.0	21.5	3.9	4.8	98.6

However, the EF (98.5) was close to the maximum EF 100 (10 mL sample: 100 μL analytical solution) obtained by exhaustive extraction. The reason of observation may be that the matrix of Cd^{2+} standard solution (water) and analytical solution (ethanol) was different, which resulted in the difference of the slopes. Table 2 provides a comparison between the proposed sample preparation method and previously applied sample preparation method for trace detection of cadmium ions [37–41].

Validation of the method

The concentration of cadmium ions obtained by the applied sample preparation method was compared to the certified reference material. For this reason, the concentration of the cadmium ions was monitored at optimized conditions in sea food mix (standard reference material) which was reported by the food Survey of Iran. The standard reference material was digested with 6 mL of HCl [37% (v/v)] and 2 mL of HNO_3 [65% (v/v)] in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W and 8 min at 550 W followed by venting for 8 min. The digestion residue was then diluted with double-distilled water [42]. According to the data in Table 3, the measured mean value is not significantly different from the certified value [43]. Therefore, SFODME can be used as a reliable sample preparation method for separation and trace detection of cadmium ions in food samples.

Determination of cadmium in food and water samples

For accessing the applicability of the proposed method for trace detection of cadmium ions in the real samples with different matrices containing varying amount of potentially interfering ions, the method was applied to pre-concentration, extraction and trace monitoring of cadmium ions in 10 mL of food and water samples. The results are shown in Table 4. The obtained results indicated that the applied sample preparation method can be reliably used for the trace detection of cadmium ions in different matrices.

Furthermore, to evaluate the efficiency of the proposed method for analysis of cadmium ions in water samples, three types of water samples including tap water, seawater

and river water were evaluated. The result is presented in Table 4.

We check the accuracy of the method by spiked addition method, and after analysis of target ions by the proposed method, the closeness of quantity value obtained by measurement and the true value in real samples was presented by relative recovery (RR%).

RR is calculated as follows:

$$\text{RR} (\%) = (C_{\text{found}} - C_{\text{real}} / C_{\text{added}}) \times 100$$

where C_{founded} , C_{real} and C_{added} are the concentrations of analyte after addition of a known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of a known amount of standard, which was spiked to the real sample, respectively.

To evaluate the precision of the obtained data for real samples analysis, we used from RSD %. All analysis of real samples to determine of RSD was monitored in triplicate.

Conclusions

The coupling of SFODME with FI-FAAS was applied for pre-concentration and trace determination of cadmium ions in food samples. The proposed procedure is low cost, very simple and benefits from a very low limit of detection. The short extraction time is related to the infinitely large surface area between organic solvent and aqueous phase after formation of cloudy solution. Therefore, complex formation/transfer from aqueous phase to organic solvent is fast. Moreover, it uses extraction solvent with lower toxicity instead of solvent with high toxicity in DLLME (chlorinated solvents) [44]. The limit of detection, relative standard deviation (%) and enrichment factor of the method was 0.02, 3.7 and 98.5%, respectively. In summary, the main benefits of the system were enhancement of instrument sensitivity, minimum organic solvent consumption, removing of matrix constituent, low cost and high enrichment factor. Finally, the present study may provide a reliable and simple method for cadmium ion detection at trace levels in different food and water samples.

Acknowledgement The authors gratefully acknowledge the Research Council of Sabzevar University of medical Science for the financial support (Project No. 94050).

References

- J. Abolhasani, M. Behbahani, Application of 1-(2-pyridylazo)-2-naphthol-modified nanoporous silica as a technique in simultaneous trace monitoring and removal of toxic heavy metals in food and water samples. *Environ. Monit. Assess.* **187**, 1–12 (2015)
- M. Behbahani, A. Ali Akbari, M.M. Amini, A. Bagheri, Synthesis and characterization of pyridine-functionalized magnetic mesoporous silica and its application for preconcentration and trace detection of lead and copper ions in fuel products. *Anal. Methods* **6**, 8785–8792 (2014)
- F. Omid, M. Behbahani, S.J. Shahtaheri, S. Salimi, Trace monitoring of silver ions in food and water samples by flame atomic absorption spectrophotometry after preconcentration with solvent-assisted dispersive solid phase extraction. *Environ. Monit. Assess.* **187**, 1–10 (2015)
- United States Environmental Protection Agency, *National Primary Drinking Water Standards* (United States Environmental Protection Agency, Washington, DC, 2003)
- N. Jalbani, M. Soylak, Separation–preconcentration of nickel and lead in food samples by a combination of solid–liquid–solid dispersive extraction using SiO₂ nanoparticles, ionic liquid-based dispersive liquid–liquid micro-extraction. *Talanta* **131**, 361–365 (2015)
- Z.A. AlOthman, M.A. Habila, S.M. Alfadul, E. Yilmaz, M. Soylak, A green, novel and simple microprecipitation technique for separation and preconcentration of cadmium with 1-(2-thiazolylazo)-2-naphthol in food samples and determination by microsampling flame atomic absorption spectrometry. *Anal. Methods* **8**, 3545–3549 (2016)
- S. Khan, M. Soylak, T. Gul Kazi, A simple ligandless microextraction method based on ionic liquid for the determination of trace cadmium in water and biological samples. *Toxicol. Environ. Chem.* **95**, 1069–1079 (2013)
- P. Askari, A. Faraji, G. Khayatian Sajjad Mohebbi, Effective ultrasound-assisted removal of heavy metal ions As(III), Hg(II), and Pb(II) from aqueous solution by new MgO/CuO and MgO/MnO₂ nanocomposites. *J. Iran. Chem. Soc.* **14**, 613–621 (2017)
- D. Kong, F. Yan, D. Shi, Q. Ye, Z. Han, L. Chen, L. Wang, Carbon dots: synthetic methods and applications as fluorescent probes for the detection of metal ions, inorganic anions and organic molecules. *J. Iran. Chem. Soc.* **12**, 1841–1857 (2015)
- T. Madrakian, A. Afkhami, N. Rezvani-jalal, M. Ahmadi, Removal and preconcentration of lead(II), cadmium(II) and chromium(III) ions from wastewater samples using surface functionalized magnetite nanoparticles. *J. Iran. Chem. Soc.* **11**, 489–498 (2014)
- M. Salarian, A. Ghanbarpour, M. Behbahani, S. Bagheri, A. Bagheri, A metal-organic framework sustained by a nanosized Ag₁₂ cuboctahedral node for solid-phase extraction of ultra traces of lead(II) ions. *Microchim. Acta* **181**, 999–1007 (2014)
- X. Guo, M. He, B. Chen, B. Hu, Phase transfer hollow fiber liquid phase microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for the determination of trace heavy metals in environmental and biological samples. *Talanta* **101**, 516–523 (2012)
- B. Hu, M. He, B. Chen, L. Xia, Liquid phase microextraction for the analysis of trace elements and their speciation. *Spectrochim. Acta. B* **86**, 14–30 (2013)
- M. Behbahani, P. Ghareh Hassanlou, M.M. Amini, F. Omid, A. Esrafil, M. Farzadkia, A. Bagheri, Application of solvent-assisted dispersive solid phase extraction as a new, fast, simple and reliable preconcentration and trace detection of lead and cadmium ions in fruit and water samples. *Food Chem.* **187**, 82–88 (2015)
- M. Behbahani, A. Esrafil, S. Bagheri, S. Radfar, M. Kalate Bojdi, A. Bagheri, Modified nanoporous carbon as a novel sorbent before solvent-based de-emulsification dispersive liquid–liquid microextraction for ultra-trace detection of cadmium by flame atomic absorption spectrophotometry. *Measurements* **51**, 174–181 (2014)
- M. Behbahani, F. Najafi, S. Bagheri, M. Kalate Bojdi, M. Salarian, A. Bagheri, Application of surfactant assisted dispersive liquid–liquid microextraction as an efficient sample treatment technique for preconcentration and trace detection of zonisamide and carbamazepine in urine and plasma samples. *J. Chromatogr. A* **1308**, 25–31 (2013)
- C. Özdemir, Ş. Saçmacı, Ş. Kartal, M. Saçmacı, Determination of gold and palladium in environmental samples by FAAS after dispersive liquid–liquid microextraction pretreatment. *J. Ind. Eng. Chem.* **20**, 4059–4065 (2014)
- Ş. Saçmacı, Ş. Kartal, S. Dural, Dispersive liquid–liquid microextraction procedure for the determination of palladium by flame atomic absorption spectroscopy. *J. Braz. Chem. Soc.* **23**, 1033–1040 (2012)
- E. Yilmaz, M. Soylak, Solid phase extraction of Cd, Pb, Ni, Cu, and Zn in environmental samples on multiwalled carbon nanotubes. *Environ. Monit. Assess.* **186**, 5461–5468 (2014)
- F. Marahel, M. Ghaedi, A. Shokrollahi, M. Montazerzohori, S. Davoodi, Sodium dodecyl sulfate coated poly (vinyl) chloride: an alternative support for solid phase extraction of some transition and heavy metals. *Chemosphere* **74**, 583–589 (2009)
- M.R. Nabid, R. Sedghi, M. Behbahani, B. Arvan, M.M. Heravi, H. Abdi Oskooie, Application of poly 1,8-diaminonaphthalene/multiwalled carbon nanotubes-COOH hybrid material as an efficient sorbent for trace determination of cadmium and lead ions in water samples. *J. Mol. Recognit.* **27**, 421–428 (2014)
- A. Bagheri, M. Behbahani, M.M. Amini, O. Sadeghi, M. Taghizade, L. Baghayi, M. Salarian, Simultaneous separation and determination of trace amounts of Cd(II) and Cu(II) in environmental samples using novel diphenylcarbazine modified nanoporous silica. *Talanta* **89**, 455–461 (2012)
- M. Hadj Youcef, T. Benabdallah, H. Reffas, Cloud point extraction studies on recovery of nickel(II) from highly saline sulfate medium using salicylideneaniline mono-Schiff base chelating extractant. *Sep. Purif. Technol.* **149**, 146–155 (2015)
- L. Zhao, S. Zhong, K. Fang, Z. Qian, J. Chen, Determination of cadmium(II), cobalt(II), nickel(II), lead(II), zinc(II), and copper(II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry. *J. Hazard. Mater.* **239–240**, 206–212 (2012)
- K. Pytlakowska, V. Kozik, M. Dabioch, Complex-forming organic ligands in cloud-point extraction of metal ions: a review. *Talanta* **110**, 202–228 (2013)
- M.R. Khalili Zanjani, Y. Yamini, S. Shariati, J.A. Jönsson, A new liquid-phase microextraction method based on solidification of floating organic drop. *Anal. Chim. Acta* **585**, 286–293 (2007)
- H. Farahani, M.R. Ganjali, R. Dinarvand, P. Norouzi, Screening method for phthalate esters in water using liquid-phase microextraction based on the solidification of a floating organic microdrop combined with gas chromatography–mass spectrometry. *Talanta* **76**, 718–723 (2008)
- M.C. López-Blanco, S. Blanco-Cid, B. Cancho-Grande, J. Simal-Gándara, Application of single-drop microextraction and comparison with solid-phase microextraction and solid-phase extraction for the determination of α - and β -endosulfan in water samples by gas chromatography–electron-capture detection. *J. Chromatogr. A* **984**, 245–252 (2003)
- H.R. Sobhi, Y. Yamini, A. Esrafil, M. Adib, Extraction and determination of 2-pyrazoline derivatives using liquid phase

- microextraction based on solidification of floating organic drop. *J. Pharm. Biomed. Anal.* **48**, 1059–1063 (2008)
30. H.R. Sobhi, Y. Yamini, A. Esrafil, R.H.H.B. Abadi, Suitable conditions for liquid-phase microextraction using solidification of a floating drop for extraction of fat-soluble vitamins established using an orthogonal array experimental design. *J. Chromatogr. A* **1196**, 28–32 (2008)
 31. M. Rezaee, Y. Yamini, A. Khanchi, M. Faraji, A. Saleh, A simple and rapid new dispersive liquid–liquid microextraction based on solidification of floating organic drop combined with inductively coupled plasma-optical emission spectrometry for preconcentration and determination of aluminium in water samples. *J. Hazard. Mater.* **178**(1), 766–770 (2010)
 32. Y. Yamini, M. Rezaee, A. Khanchi, M. Faraji, A. Saleh, Dispersive liquid–liquid microextraction based on the solidification of floating organic drop followed by inductively coupled plasma-optical emission spectrometry as a fast technique for the simultaneous determination of heavy metals. *J. Chromatogr. A* **1217**(16), 2358–2364 (2010)
 33. F. Kamarei, H. Ebrahimzadeh, Y. Yamini, Optimization of ultrasound-assisted emulsification microextraction with solidification of floating organic droplet followed by high performance liquid chromatography for the analysis of phthalate esters in cosmetic and environmental water samples. *Microchem. J.* **99**(1), 26–33 (2011)
 34. S. Dadfarnia, A.M. Salmanzadeh, A.M. Haji Shabani, A novel separation/preconcentration system based on solidification of floating organic drop microextraction for determination of lead by graphite furnace atomic absorption spectrometry. *Anal. Chim. Acta* **623**, 163–167 (2008)
 35. S. Dadfarnia, A.M.H. Shabani, E. Kamranzadeh, Separation/preconcentration and determination of cadmium ions by solidification of floating organic drop microextraction and FI-AAS. *Talanta* **79**, 1061–1065 (2009)
 36. M. Ghambarian, Yamini Y, Khalili-Zanjani MR, Yazdanfar N, Esrafil A, Preconcentration and speciation of arsenic in water specimens by the combination of solidification of floating drop microextraction and electrothermal atomic absorption spectrometry. *Talanta* **81**, 197–201 (2010)
 37. M. Behbahani, M. Barati, M. Kalate Bojdi, A.R. Pourali, A. Bagheri, N. Akbari Ghareh Tapeh, A nanosized cadmium(II)-imprinted polymer for use in selective trace determination of cadmium in complex matrices. *Microchim. Acta* **180**, 1117–1125 (2013)
 38. M.R. Nabid, R. Sedghi, A. Bagheri, M. Behbahani, M. Taghizadeh, H. Abdi Oskooie, M.M. Heravi, Preparation and application of poly(2-amino thiophenol)/MWCNTs nanocomposite for adsorption and separation of cadmium and lead ions via solid phase extraction. *J. Hazard. Mater.* **203–204**, 93–100 (2012)
 39. P. Liang, J. Li, X. Yang, Cloud point extraction preconcentration of trace cadmium as 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone complex and determination by flame atomic absorption spectrometry. *Microchim. Acta* **152**, 47–51 (2005)
 40. Silva E. dos Santos, L. Oliveira Correia, L. Oliveira dos Santos, Vitor dos Santos, E. Vieira, V. Azevedo Lemos, Dispersive liquid-liquid microextraction for simultaneous determination of cadmium, cobalt, lead and nickel in water samples by inductively coupled plasma optical emission spectrometry. *Microchim. Acta* **178**, 269–275 (2012)
 41. C. Arpa Sahin, I. Durukan, Ligandless-solidified floating organic drop microextraction method for the preconcentration of trace amount of cadmium in water samples. *Talanta* **85**, 657–661 (2011)
 42. A.B. Yilmaz, Levels of heavy metals (Fe, Cu, Ni, Cr, Pb, and Zn) in tissue of *Mugil cephalus* and *Trachurus mediterraneus* from Iskenderun Bay, Turkey. *Environ. Res.* **92**, 277–281 (2003)
 43. Linsinger TPJ (2005) Comparison of measurement results with the certified value, ERM Application Note 1. <http://www.erm-crm.org>
 44. J.G. March, V. Cerdà, A novel procedure for phase separation in dispersive liquid-liquid microextraction based on solidification of the aqueous phase. *Talanta* **156–157**, 204–208 (2016)