Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.20828

124 (2018) 193–201
August

Development of cloud point extraction preconcentration of cadmium and lead in solid samples using flame atomic absorption spectrometry

Zekeriyya Bahadır[a,*], Murat Yazar[b], Süreyya Oğuz Tümay[c], Hüseyin Serencam[d], Hakan Bektaş[a], Celal Duran[b]

[a]*Department of Chemistry, Faculty of Arts and Sciences, Giresun University, Giresun, Turkey, Tel. +90 5534479358, Fax +904543101477, email: zekeriyyabahadir@gmail.com, zekeriyya.bahadir@giresun.edu.tr (Z. Bahadur), hakan.bektas@giresun.edu.tr (H. Bektaş)*

[b]*Department of Chemistry, Faculty of Sciences Karadeniz Technical University, Trabzon, Turkey, email: ktumurat61@hotmail.com (M. Yazar), cduran@ktu.edu.tr (C. Duran)*

[c]*Department of Chemistry, Gebze Technical University, Gebze, Kocaeli, Turkey, email: sotumay@gtu.edu.tr (S.O. Tümay),*

[d]*Department of Food Engineering, Faculty of Engineering , Bayburt University, Bayburt, Turkey, email: hserencam@bayburt.edu.tr (H. Serencam)*

Received 1 February 2018; Accepted 8 August 2018

ABSTRACT

2-[(6-Morpholin-4-ylpyridin-3-yl)amino]-N′-(4-oxo-3-phenyl-1,3thiazolidin-2-ylidene) acetohydrazide (MPAPTAH) was first used in a cloud point extraction procedure to determine the cadmium and lead ions in solid samples. Triton X-114 was used as a mixed micellar medium. The optimal extraction parameters (e.g. surfactant concentrations, amount of ligand, pH etc.) were evaluated. The optimum experimental conditions for Cd and Pb ions during the extraction procedure were carried out with 0.7 mg of MPAPTAH agent, 1.0 mL 0.2% (w/v) of the surfactant, a pH of 8.0. Under the best analytical parameters, the detection limit (LOD) for Cd(II) and Pb(II) ions were found to be 0.6 μg L^{-1} and 1.91 μg L^{-1}, while the relative standard deviation (RSD) was taken as 2.78 and 2.86%, respectively. Preconcentration factor (PE) of 50 was obtained from using 50 mL of the sample volume for both ions. The accuracy of the method was tested through analysis of Pb^{2+} and Cd^{2+} in certified reference material (CRM Sandy Soil C). The interference effect of certain cations and anions were also investigated. The recoveries of the analyte ions were almost quantitative in the presence of all the interfering ions. Afterwards, the developed method was successfully applied to find lead and cadmium in real solid samples, including black tea, tobacco, and chili pepper.

Keywords: Triton X-114; Nonionic surfactant; Cloud point extraction; Lead; Cadmium

---

1. Introduction

Toxic heavy metal environmental pollution has become an increasing concern on the ground in which there is a significant source of existing toxic pollutes in the ecosystem [1–3]. These metals accumulate in living organisms and pose dangerous risks. Cadmium is one of the concrete example of toxic heavy metals that is extensively used across modern industry, especially in plastics, electroplating, paint [4,5]. Cigarette smoke and food are the primary sources of cadmium exposure for human beings [6]. Various studies have noted a significant accumulation of cadmium in human livers, lungs and kidneys [7]. Cadmium is also carcinogenic and is known to play a vital role in the worsening of cardiovascular diseases, hypertension, and muscular craps [8]. Lead (Pb) is another toxic heavy metal that accumulates gradually in the body over one's lifetime [9,10]. Anthropogenic activities such as burning fossil fuels and mining activities, have become a source of lead pollution in our environment. The risks tied to lead exposure through food have negative effects on human health [11]. Lead affects human reproductive, neurological,

---

*Corresponding author.

and renal systems [12,13]. Chronic symptoms of lead poisoning include vomiting, dizziness, nausea, diarrhea, and appetite loss [14].

These adverse effects mean that the smallest presence of cadmium and lead in the environment, food, and biological systems of human beings has also an important impact [15,16]. Inductively coupled plasma-mass spectrometry ICP-MS [17] and graphite furnace atomic absorption spectrometry (GFAAS) [18] are two examples of various research techniques currently utilized to determine heavy metals at trace levels, each of which is time-consuming and expensive. Flame atomic absorption spectrometry (FAAS) is one of the alternatives utilized for environmental samples on the ground and this research technique is relatively convenient, fast, simple, and relatively low at cost [19–21]. Unfortunately, for water and food samples, trace element concentration levels are low and matrix interference would not be always eliminated. Therefore, examination for trace element amounts has to be carried out by using separation-pre-concentration methodology prior to their analysis. The most common usage of these techniques includes Pb^{2+} and Cd^{2+}, liquid–liquid extraction (LLE) [22], co precipitation [23,24], solid phase extraction [25,26], and cloud point extraction (CPE) [27,28]. Cloud point extraction (CPE) is based on the micelle-mediated process in aqueous media, and involves phase separation after increasing the temperature or adding a chelating agent [29]. This extraction technique requires the mixing either a cationic/anionic surfactant with non-ionic surfactants or the formation of covalent hydrophobic chelates of the respective metal ion with suitable reagents. Triton X-114 was selected as the non-ionic surfactant due to its commercial availability, which is relatively low in toxicity. CPE is an eco-friendly method for the reason that surfactants are not toxic and non-volatile when compared with organic solvents used in conventional extraction procedures. This method is also cost-effective and has a high extraction efficiency in relation to sample preparation [30,31].

In the present work, 2-[(6-morpholin-4-ylpyridin-3-yl) amino]-N′-(4-oxo-3-phenyl-1,3-thiazolidin-2-ylidene) acetohydrazide was used as a sensitized complexing agent for the cloud point extraction (CPE) pre-concentration of Cd(II) and Pb(II). Triton X-114 was established as a surfactant in basic media. Factors influencing the efficiency of CPE were studied, including the pH, Triton X-114, ligand concentrations, incubation time/temperature, centrifugation rate, and time. The CPE method presented throughout this research was straight forward and selective in accurately determining Cd(II) and Pb(II) in tobacco, tea, and chili pepper samples without interferences.

2. Experimental evaluations

2.1. Reagents and apparatus

In this study, analytical grade reagents were used. Ultrapure water was also utilized. High purity stock solutions of the Cd(II) and Pb(II) ions (1000 mg L^{-1}) were obtained from Sigma (St. Louis, MO, USA). Working standard solutions of these elements were diluted before their usage. 0.1 mol L^{-1} HNO_3 and NaOH (obtained from Merck, Germany) were used for pH adjustment. We prepared a stock 1% (w/v) solution of Triton X-114 by dissolving 1 g of Triton X-114 (Sigma–Aldrich, USA) in hot distilled water total volume adjusted to 100 mL. 2-[(6-morpholin-4-ylpyridin-3-yl)amino]-N′-(4-oxo-3-phenyl-1,3-thiazolidin-2 ylidene) acetohydrazide (MPAPTAH) [32] was utilized for the first time as the chelating reagent. Its solution was prepared (0.07% (w/v)) in ethanol and dimethyl sulfoxide (5:1). In order to cross-check the accuracy of the presented method, we analyzed CRM-SA-C Sandy Soil C certified reference material (obtained form High-Purity Standard Inc. Charleston, SC, USA).

All absorbance measurements were conducted to use an A Perkin Elmer AAnalyst 400 flame atomic absorption spectrometer (Waltham, United States) with a deuterium lamp for background correction. Hollow-cathode cadmium (6 mA) and lead (460 mA) lamps were utilized as a radiation source and operated at 228.80 and 283.31 nm wavelengths in turn. The flame composition included acetylene and air with flow rate of 2.5 and 17.0 L/min for the working elements. A digital pH-meter (model HI 2221, Hanna) equipped with a glass combination electrode was used to measure the aqueous solution. A Sigma 3-16P model centrifuge (Sigma laborzentrifugen GmbH, Germany) was benefited to accelerate the phase separation process. Ultra-pure water was obtained from using the Merck-Millipore Direct-Q 8UV system (Darmstadt, Germany). Solid samples digestion was performed in a Milestones Ethos D digest microwave system (Milestore Inc., Italy) with a closed vessel.

2.2. Procedure of CPE

An aliquot of 50 mL sample solution containing 5.0 µg L^{-1} Cd^{2+} and 50 µg L^{-1} Pb^{2+} were poured into a 50 mL plastic tube. The pH of the solution was then adjusted to 8.0 with 0.1 mol L^{-1} NaOH/HNO_3. 1.0 mL 0.7 mg of the MPAPTAH solution and 1.0 mL 0.2% (w/v) of the Triton X-114 solution were added into the tube. The resultant solution was kept in a thermo stated water bath at 45°C for 15 min with thermometer controller. The phase separation was accelerated by centrifuging it for 5 min at 2000 rpm. The tubes were cooled in an ice-bath in which the surfactant-rich phase became viscous for 5 min; this aqueous phase was then decanted. In order to reduce the viscosity of the surfactant-rich, 1.0 mL of acidic ethyl alcohol (0.5 mol L^{-1} HNO_3) was added. The solution with the Cd^{2+} and Pb^{2+} ions was determined using FAAS by conventional aspiration. The duplicate blanks of both complexing reagents were simultaneously submitted without additional samples and standards.

A summary of the CPE-FAAS method is shown in Fig. 1.

2.3. Applications in real samples

We applied the proposed method to determine Pb(II) and Cd(II) in various solid samples including tobacco, chili pepper, and black tea obtained from a local market in Trabzon,Turkey. 0.5 g of each was put into a Teflon vessels and treated with 8 mL of HNO_3 and 2 mL of H_2O_2. To perform digestion with the microwave system [33], 6-min cycles at 45 bar were applied at 250 W, 400 W, 650 W, and 250 W. Ventilation was 10-min duration. After microwave digestion, the mixtures evaporated and dried. Then, 15–20 mL of distilled water was added and then filtered by means of blue

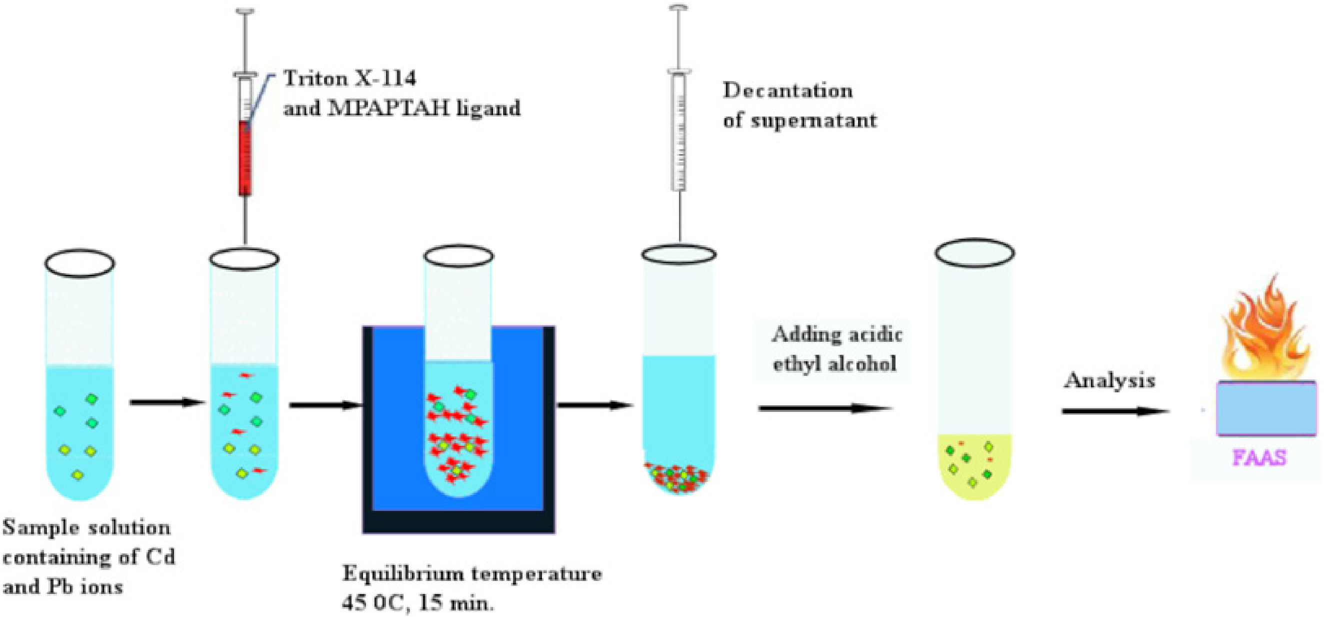

Fig. 1. Scheme and analytical procedure for the simultaneous determination of lead and cadmium using the developed CPE-FAAS system.

ribbon filter paper (Dassel, Germany). Finally, this sample solution was diluted down to 50.0 mL and the procedure described in section 2.2 was applied.

The digestion of CRM-SA-C Sandy Soil C (0.1 g) certified standard reference material was carried out with 2.0 mL of HNO_3, 6.0 mL of HCl, 1.0 mL of HF and 2.0 mL of H_2O_2 in a closed microwave digestion system. The solution was evaporated to near dryness and then filtrated. The residue was completed using a 25 mL (stock solution) volumetric flask with ultra pure water. A 2.5 mL aliquot (for Cd and Pb) was diluted down to a final volume of 50 mL, followed by being run through the CPE procedure. Likewise, a blank extraction (without sample) underwent the complete procedure.

3. Results and discussion

3.1. Effect of pH

The pH should be adjusted before performing CPE in order to ensure that the neutral molecular form the analytes. In this work, the effect of pH on the extraction efficiency of cadmium (5.0 ng mL^{-1}) and lead (50.0 ng mL^{-1}) was examined for pH values varying from 2.0 to 10.0 as shown in Fig. 2. The extraction efficiency appeared to be high for both Cd^{2+} and Pb^{2+} at pH 8.0. The extraction efficient at pH < 8.0 is very low which is probably due to protonation of the ligand and complex formation. The decrease in extraction at pH > 8.0 is potentially because of the hydrolysis of lead and cadmium cations [34]. Thus, pH 8.0 was established as the optimum pH value for maximum extraction.

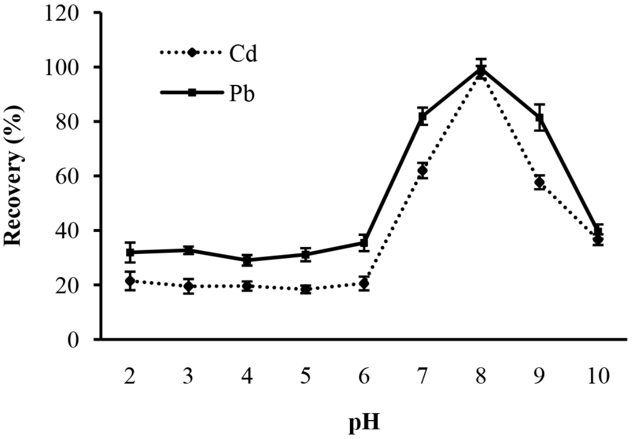

Fig. 2. The influence of the pH on the recovery of lead and cadmium ions. Conditions: water sample, 50 mL; MPAPTAH, 0.70 mg; 1.0 mL of 0.2 % (w/v) Triton X-114; equilibrium temperature 45°C; equilibrium time of 15 min; centrifugation time of 5 min; centrifugation rate of 2000 rpm). Error bar: mean of three experiments ± standard deviation (n = 3).

3.2. Effects of concentrations of MPAPTAH

Optimizing the concentration of the chelating agent is important in the high recovery of the analyte ions from aqueous media. The ligand that forms this complex must be sufficiently hydrophobic and have a high partition coefficient as well as be able to quickly and quantitatively the complex with minimum excess. In order to estimate the optimum ligand quantity, different amounts of the MPAPTAH in the 0.0–2.0 mg range were examined for the pre-concentration of the 50.0 mL sample solution, including analyte ions. Under optimal conditions, the recoveries of Cd^{2+} and Pb^{2+} ions were 32–42 % without adding MPAPTAH ligand. This showed that the quantitative recoveries of both ions ligand are necessary. As can be seen from Fig. 3, the maximum extraction efficiency of cadmium and lead ions were

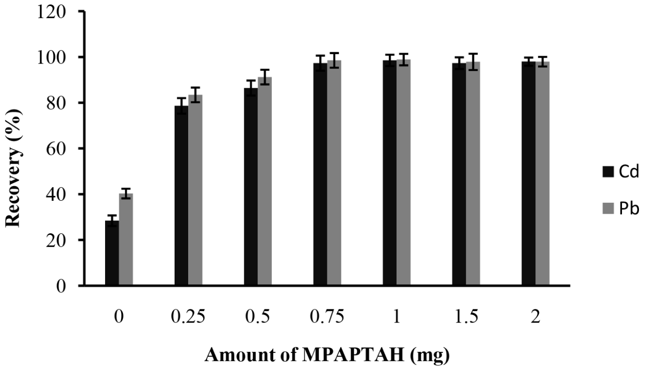

Fig. 3. The effect of MPAPTAH concentration on the extraction efficiency of cadmium and lead ions in surfactant-rich phase. Conditions: water sample, 50.0 mL; 1.0 mL, 0.2 % (w/v) Triton X-114; equilibrium temperature of 45°C; equilibrium time 15 min; centrifugation time of 5 min, (n = 3).

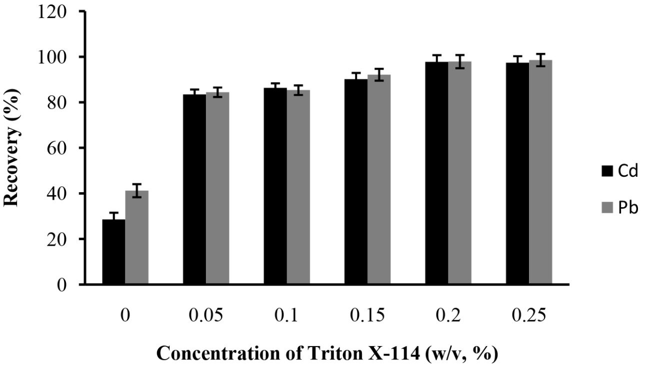

Fig. 4. The effect of Triton X-114 concentration extraction efficiency of cadmium in surfactant-rich phase. Conditions: water sample, 50.0 mL; MPAPTAH, 0.75 mg; equilibrium temperature 45°C; equilibrium time 15 min; centrifugation rateand time: 2000 rpm and 5 min) (n = 3).

achieved at 0.7 mg of MPAPTAH and then remained constant. Hence, MPAPTAH amount of 0.7 mg was selected for further study.

3.3. Effects of surfactant concentration

The concentration of surfactant used in CPE is one of the key factors affecting the extraction efficiency. Triton X-114 is probably the best choice for the CPE due to its low cloud point temperature (23–26°C), its high density of the surfactant rich phase, and its low toxicity [35]. The high density of the surfactant rich phase also facilitates phase separation by centrifugation. The effect of the Triton X-114 concentration on the quantitative recoveries of Pb(II) and Cd(II) were examined in the range of 0.0–0.35% (w/v). As can be seen in Fig. 4, the recovery is maximum as the Triton X-114 concentration was 0.2% (w/v). At lower concentrations, the extraction efficiency of complexes was low. This is due to the inadequacy of the assemblies that entrap the hydrophobic complex quantitatively. We thus selected a concentration of 0.2% (w/v) of Triton X-114 for the following experiments.

3.4. Effects of equilibrium temperature and time

In the cloud point extraction, the equilibration temperature is an important parameter for achieving micelles and easy phase separation. It has been reported that longer equilibration times (of more than 30 min) do not have any significant effect on the extraction parameters [36]. An equilibration time of 15-minute duration was therefore selected in order to obtain satisfactory extraction in this work. The effect of the equilibration temperature was studied with a range of 30–60°C. The results show that an equilibration temperature of 45°C is adequate to achieve high quantitative extraction efficiency for both Cd(II) and Pb(II) ions.

3.5. Effect of centrifugation rate and time

The performance of the CPE procedure, which was based on the centrifugation speed of 1000–3000 rpm and of centrifugation time between 5–30 min, was also investigated. For the phase separation, a centrifugation rate of 2000 rpm and centrifugation time of 5-min were found to be optimum.

3.6. Effect of sample volume

Sample volume plays a key role in obtaining a higher enrichment factor. Thus, 15–50 mL sample volume range containing 0.25 µg of cadmium and 0.5 µg of lead ions were extracted according to the procedure described in Section 2.2. The recovery values of the analyte ions increased with increasing the volume of the sample solution. A sample volume below 50.0 mL did not affect the recovery values of the analyte ions. The optimum sample volume was established at 50 mL for the quantitative determination of Pb(II) and Cd(II) ions under optimum experimental conditions.

3.7. Interferences of co-existing ions

In order to demonstrate the performance of the developed cloud point extraction method, the influence of the common co-existing ions in the matrices were investigated for the recovery of Cd^{2+} and Pb^{2+} ions. For this purpose, in the presented procedure, 50.0 mL of the solution containing 0.5 µg of lead, 0.25 µg cadmium and various amounts of interfering ions were treated by using the recommended procedure. The results are provided in Table 1. A variation of higher than ± 5% recovery was regarded as an interference. As shown below, interference ion concentration were recorded as having no stastitical significance throughout the study.

3.8. Analytical merit of the CPE

In this part of the work, we present the analytical characteristic data of the CPE-FAAS for Cd(II) and Pb(II). A good linear dynamic range of the presented method for Cd and Pb was found to be in the concentration range of 5–240 µg L^{-1} and 1–100 µg L^{-1} at optimal parameters. The limit of detection (LOD) is defined as the concentration equivalent to

Table 1
The tolerance limits of interfering species in the determination of 5.0 ng mL^{-1} of Cd(II) and 50.0 ng mL^{-1} Pb(II) ions, (n = 3)

Ions	Recovery (%)		
	Conc. (mg L^{-1})	Pb(II)	Cd(II)
Na^+	5000	99 ± 4	99 ± 3
K^+	1000	98 ± 3	99 ± 5
Ca^{2+}	1000	94 ± 2	96 ± 3
Mg^{2+}	1000	94 ± 2	95 ± 2
NO_3^-	1000	95 ± 3	99 ± 4
CO_3^{2-}	1000	99 ± 5	99 ± 3
PO_4^{3-}	1000	97 ± 3	98 ± 3
NH_4^+	1000	97 ± 3	98 ± 3
Zn^{2+} Ni^{2+} Al^{3+} Co^{2+} Cu^{2+} V^{5+} Mn^{2+} Cr^{3+} Fe^{3+}	25	96 ± 2	100 ± 5
Mixed*		95 ± 2	99 ± 3

* 5000 mg L^{-1} Na^+, 8000 mg L^{-1} Cl^-, 2000 mg L^{-1} NO_3^-, 250 mg L^{-1} Ca^{2+}, K^+, Mg^{2+}, CO_3^{2-} , SO_4^{2-} , NH_4^+ ve PO_4^{3-}, 10 mg L^{-1}, Al^{3+}, Co^{2+}, Cu^{2+}, V^{5+}, Mn^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, 8000 mg L^{-1} Cl^-, 2000 mg L^{-1} NO_3^-, 250 mg L^{-1} Ca^{2+}, K^+, Mg^{2+}, CO_3^{2-} , SO_4^{2-} , NH_4^+ and PO_4^{-3}

Table 2
Addition recovery/test procedure for solid samples (n = 3)

Sample	Pb			Cd		
	Added (μg)	Found (μg)	Recovery (%)	Added (μg)	Found (μg)	Recovery (%)
Tobacco	0	<LOD	–	0	0.59	–
	1.0	0.94 ± 0.03	94 ± 2	0.5	1.07 ± 0.04	96 ± 3
	2.0	1.90 ± 0.06	95 ± 2	1.0	1.54 ± 0.06	95 ± 3
Black tea	0	<LOD	–	0	<LOD	–
	1.0	0.98 ± 0.03	98 ± 3	0.5	0.47 ± 0.02	94 ± 2
	2.0	1.96 ± 0.05	98 ± 3	1.0	0.96 ± 0.04	96 ± 3
Chili pepper	0	<LOD	–	0	<LOD	–
	1.0	1.10 ± 0.04	101 ± 4	0.5	0.52 ± 0.03	104 ± 5
	2.0	2.02 ± 0.07	102 ± 4	1.0	1.04 ± 0.04	104 ± 5

LOD: Limit of detection

three times the standard deviation of 10 measurements of the blank after preconcentration was found to be 1.91 μg L^{-1} for Pb(II) and 0.60 μg L^{-1} for Cd(II). The method's precision was calculated as the relative standard deviation (R.S.D) of 10 replicate measurements executed with 5.0 μg L^{-1} Cd(II) and 50.0 μg L^{-1} Pb(II) solutions and found as 2.78% and 2.86% for cadmium and lead, respectively. The preconcentration factor (PF) was calculated as 50 for the both ions. It was defined as the beginning volumes (50 mL) of the surfactant-rich ($[V]_b$) and final diluted surfactant-rich volume (1 mL) s ($[V]_f$) using Eq. (1):

$$PF = \frac{[V]_b}{[V]_f} \tag{1}$$

As the results of this research illustrate, the presented method has a relative low dedection limit which makes it appropriate for Pb and Cd trace analysis in enviornmental samples. The enhancement factor (EF) was calculated. The ratio of the slopes of calibration graphs with and without pre-concentration is determined. The EF was found to be 42 and 45 for cadmium and lead ions, respectively.

Table 3
Determination of lead and cadmium in different solid samples

Concentration (μg g^{-1})		
Samples	Cadmium	Lead
Tobacco	1.18 ± 0.05	<LOD
Black tea	<LOD	<LOD
Chili pepper	<LOD	<LOD

3.9. Sample determination

In order to test the reliability of the proposed method, the determination of Pb(II) and Cd(II) was applied to 0.5 g tobacco, chili pepper, and black tea. Reliability was checked by analysis spiking at different amount of cadmium and lead. There is a good correspondence between the added and found levels of analytes for all samples in Table 2. All the results were displayed as μg/g in Table 3. In order to verify the accuracy of the CPE procedure, CRM-C-Sandy Soil C was used as a standard reference material. In the CRM, the certified amount of lead is 120 ± 8 µg g^{-1}, and the certified amount of cadmium is 109 ± 8 µg g^{-1}. The obtained values using CPE–FAAS method were 113.9 ± 3.2 µg g^{-1} and 103.3 ± 2.9 µg g^{-1}, for Pb^{2+} and Cd^{2+} respectively, which correspond well with the certified concentrations. The obtained results showed that a combination of CPE with FAAS is useful for the simultaneous determination of trace amounts of Cd(II) and Pb(II) ions in black tea, tobacco, and chili pepper samples.

4. Comparison with other methods

The analytical outputs of the proposed CPE-FAAS method is compared with some of the literature reported works for the preconcentration and determination of lead and cadmium. In literature survey, the ligands such as 8-hydroxyquinoline, 1-phenylthiosemicarbazide etc. have been performed for the intersted metals in cloud point extraction, which are showed in Table 4. In our work, 2-[(6-morpholin-4-ylpyridin-3-yl)amino]-N′-(4-oxo-3-phenyl-1,3 thiazolidin-2 ylidene) acetohydrazide was used first time as neutral hydrophobic complexing agent for the cadmium and lead ions. The proposed methodology has also several advantages including good linear range, low detection limits (except ref. 37, 38 and 40), high sensitivity, low cost, rapid, inexpensive and nonpolluting alternative to other preconcentration techniques.

5. Conclusion

The separation and determination of cadmium and lead in environmental samples, become crucial for the analytical chemistry, due to they are a highly toxic substance and have various forms in the natural environmental. In the developed method, Cd^{2+} and Pb^{2+} ions were initially extracted by means of cloud point extraction. The combination of CPE with FAAS is a good conjunction and has been successfully used to simultaneously separation of Pb and Cd in solid samples using 5. 2-[(6-morpholin-4-ylpyridin-3-yl)amino]-N′-(4-oxo-3-phenyl-1,3-thiazolidin-2 ylidene) acetohydrazide as sensitized new complexing agent and Triton X-114 as surfactant in basic media was established. As a small amount of ligand and a low volume of solvent and of surfactant are required in this study,the methodology is environmentally friendly. The main advantage of the method is the selectivity of the ligand towards Cd(II) and Pb(II) ions at a pH 8.0 in the presence of interfere ions. The developed procedure offers a good alternative to preconcentrate of cadmium and lead in solid samples with precision, good sensitivity, and good detection limits.

Acknowledgements

The authors thank to Giresun University (Giresun, Turkey) and Karadeniz Technical University (Trabzon, Turkey) for laboratory facilities.

Table 4
Comparison of the CPE-FAAS with other methods for the determination of lead and cadmium

Method	Metal	Reagent	Surfactant	LOD (µg L^{-1})	LR (µg L^{-1})	EF/PF	Sample	Ref.
Um-CPE+FAAS[1]	Cd	8-HQ[2]	Triton X-114	0.052	1.5–200	30.5/30.3	Serum	[37]
	Pb			0.450	1.5–200	62.5/62.5		
m-CPE+FAAS[3]	Cd	Dithizone	Triton X-114	0.050	2–50	78.9/62.5	Lake water and muscle	[38]
	Pb			0.0560	2–50	84.2/62.5		
CPE+FAAS	Pb	4-PR[4]	Triton X-114	1.15	–	–/50	Ground, tap, dam, lake and waste water	[39]
CPE+FAAS	Pb	1-PTSC[5]	Triton X-114	3.42	500–10000	–/25	Environmental samples	[40]
CPE+FAAS	Cd	O-DDP[6]	Triton X-114	0.62	3–300	22/–	Hair	[41]
	Pb			2.86	10–460	43/–		
SS-CPE+FAAS[7]	Cd	Dithizone	Triton X-114	0.27	5–100	58/–	Canal and waste water	[42]
CPE+FAAS	Cd	TAN[8]	Triton X-114	0.75	5–25	15.1/	River, lake water	[43]
	Pb			4.5	50–250	19.6/		
CPE+FAAS	Pb	2-GBI[9]	Triton X-114	11	11–6000	29.6/	Cake	[44]
CPE+FAAS	Cd	Ligandless	Tween 80	1.2	–	10/	Environmental samples	[45]
	Pb			7.2		10/		
CPE+FAAS	Cd	MPAPTAH[10]	Triton X-114	0.6	1–100	42/50	Black tea, tobacco, and chili pepper	This work
	Pb			1.91	10–240	45/50		

[1] Ultrasonically modified cloud point extraction+Flame atomic absorbtion Spectrometry, [2] 8-hydroxyquinoline, [3] Modified cloud point extraction, [4] 4-(2-pyridylazo) resorcinol, [5] 1-Phenylthiosemicarbazide, [6] O,O-Diethyldithiophosphate, [7] Simultaneous single step and multistep cloud point extraction method, [8] 1-(2-thiazolylazo)-2-naphthol, [9] 2-guanidinob enzimidazole, [10] 2-[(6-Morpholin 4-ylpyridin-3-yl)amino]-N′-(4-oxo-3-phenyl-1,3 thiazolidin-2-ylidene)acetohydrazide

References

[1] E.Z. Jahromi, A. Bidari, Y. Assadi, M.R.M. Hosseini, M.R. Jamali, Dispersive liquid–liquid micro extraction combined with graphite furnace atomic absorption spectrometry Ultra trace determination of cadmium in water samples, Anal. Chim Acta, 585 (2007) 305–311.

[2] M. Chamsaz, A. Atarodi, M. Eftekhari, S. Asadpour, M. Adibi, Vortex-assisted ionic liquid micro extraction coupled to flame atomic absorption spectrometry for determination of trace levels of cadmium in real samples, J. Adv. Res., 4 (2013) 35–41.

[3] I.A.A. Mekkawy, U.M.M. Ekbal, T. Wassif, M. Naguib, Effects of cadmium on some haematological and biochemical characteristics of Oreochromis niloticus (Linnaeus, 1758) dietary supplemented with tomato paste and vitamin E, Fish Physiol. Biochem., 37 (2011) 71–84.

[4] Q. Tang, X. Tang, M. Hu, Z. Li, Y. Chen, P. Lou, Removal of Cd(II) from aqueous solution with activated Firmiana Simplex Leaf: Behaviors and affecting factors, J. Hazard. Mater., 179 (2010) 95–103.

[5] G. Kazi, A.R. Memon, H.I. Afridi, M.K. Jamali, M.B. Arain, N. Jalbani, R.A. Sarfrz, Determination of cadmium in whole blood and scalp hair samples of Pakistani male lung cancer patients by electro thermal atomic absorption spectrometer, Sci. Total Environ., 389 (2008) 270–276.

[6] I. Lopez-Garcıa, Y. Vicente-Martınez, M.H. Cordoba, Determination of lead and cadmium using an ionic liquid and dispersive liquid-liquid micro extraction followed by electro thermal atomic absorption spectrometry, Talanta, 110 (2013) 46–52.

[7] H.R. Pohl, H.G. Abadin, J.F. Risher, in: A. Sigel, H. Sigel, R.K.O. Sigel (Eds.), Neurodegenerative Diseases and Metal Ions: Metal Ions in Life Sciences, vol. 1, Wiley, Chichester, 2006, pp. 397–408.

[8] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste, Water. Res., 36 (2002) 2304–2318.

[9] O.E. Orisakwe, C.A. Maduawguna, Lead levels in paint flakes from buildings in Nigeria: a preliminary study, Toxicol. Ind. Health, 24 (2008) 539–542.

[10] M. Soylak, E. Yilmaz, Ionic liquid dispersive liquid–liquid micro extraction of lead as pyrrolidinedithiocarbamate chelate prior to its flame atomic absorption spectrometric determination, Desalination, 275 (2011) 297–301.

[11] J.L. Manzoori, M. Amjadi, J. Abulhassani, Ultra-trace determination of lead in water and food samples by using ionic liquid-based single drop micro extraction-electro thermal atomic absorption spectrometry, Anal. Chim. Acta, 644 (2009) 48–52.

[12] P.A. Meyer, M.J. Brown, H. Falk, Global approach to reducing lead exposure and poisoning, Mutat. Res., 659 (2008) 166–175.

[13] I. Al-Saleh, S. Al-Enazi, N. Shinwari, Assessment of lead in cosmetic products, Regul. Toxicol. Pharm., 54 (2009) 105–113.

[14] M.A. Gondal, M.M. Nasr, M.M. Ahmed, Z.H. Yamani, M.S. Alsalhi, Detection of lead in paint samples synthesized locally using laser-induced breakdown spectroscopy, J. Environ. Sci. Health, A., 46 (2011) 42–49.

[15] M. Soylak, A. Uzun, L. Elci, Sorbent extraction of copper, lead, nickel and cadmium ions in dialysis concentrates before their atomic absorption spectrometric determinations, Trace Elem. Electroly., 19 (2002) 15–19.

[16] V.A. Lemos, L.A. Oliveira, Ultrasound-assisted temperature-controlled ionic liquid micro extraction for the pre-concentration and determination of cadmium content in mussel samples, Food Control, 50 (2015) 901–906.

[17] N. Ashouri, A. Mohammadi, R. Hajiaghaee, M. Shekarchi, M.R. Khoshayand, Preparation of a new nano particle Cd(II)-imprinted polymer and its application for selective separation of cadmium (II) ions from aqueous solutions and determination via inductively coupled plasma optical emission spectrometry, Desal. Water Treat., 57 (2016) 14280–14289.

[18] D.J. Butcher, Advances in electro thermal atomization atomic absorption spectrometry: instrumentation, methods, and applications, Appl. Spectrosc. Rev., 41 (2006) 15–34.

[19] S.A.R. Shahamirifard, M. Ghaedi, M.R. Rahimi, S. Hajati, M. Montazerozohori, M. Soylak, Simultaneous extraction and preconcentration of Cu^{2+}, Ni^{2+} and Zn^{2+} ions using Ag nanoparticle-loaded activated carbon: Response surface methodology, Adv. Powder Technol., 27 (2016) 426–435.

[20] A.N. Anthemidis, K.-I.G. Ioannou, On-line sequential injection dispersive liquid–liquid micro extraction system for flame atomic absorption spectrometric determination of copper and lead in water samples, Talanta, 79 (2009) 86–91.

[21] S.R. Yousefi, F. Shemirani, Development of a robust ionic liquid based dispersive liquid–liquid micro extraction against high concentration of salt for pre-concentration of trace metals in saline aqueous samples: Application to the determination of Pb and Cd, Anal Chim Acta, 669 (2010) 25–31.

[22] S.S. Swain, B. Nayak, N. Devi, S. Das, N. Swain, Liquid liquid extraction of cadmium(II) from sulfate medium using phosphonium and ammonium based ionic liquids diluted in kerosene, Hydrometallurgy, 162 (2016) 63–70.

[23] Z. Bahadır, V.N. Bulut, D. Ozdes, C. Duran, H. Bektas, M. Soylak, Separation and pre-concentration of lead, chromium and copper by using with the combination coprecipitation-flame atomic absorption spectrometric determination, J. Ind. Eng. Chem., 20 (2014) 1030–1034.

[24] S. Tokalioglu, T. Oymak, S. Kartal, Coprecipitation of lead and cadmium using copper(II) mercaptobenzothiazole prior to flame atomic absorption spectrometric determination, Microchim. Acta., 159 (2007) 133–139.

[25] C. Duran, V.N. Bulut, M. Soylak, L. Elci, H.B. Sentürk, M. Tüfekci, Solid-phase extraction of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from environmental samples by flame atomic absorption spectrometry (FAAS), J. Hazard. Mater., 146 (2007) 347–355.

[26] M. Ghaedi, K. Niknam, A. Shokrollahi, E. Niknam, H.R. Rajabi, M. Soylak, Flame atomic absorption spectrometric determination of trace amounts of heavy metal ions after solid phase extraction using modified sodium dodecyl sulfate coated on alumina, J. Hazard. Mater., 115 (2008) 121–127.

[27] S. Nekouei, F. Nekouei, I. Tyagi, S. Agarwal, V.K. Gupta, Mixed cloud point/solid phase extraction of lead(II) and cadmium(II) in water samples using modified-ZnO nano powders, Process Saf. Environ. Prot., 99 (2016) 175–185.

[28] W.I. Mortada, M.M. Hassanien, A.F. Donia A.A. Shokeir, Application of cloud point extraction for cadmium in biological samples of occupationally exposed workers: relation between cadmium exposure and renal lesion, Biol. Trace Elem. Res., 168 (2015) 303–310.

[29] P. Samaddar, K. Sen, Cloud point extraction: A sustainable method of elemental preconcentration and speciation, J. Ind. Eng. Chem., 20 (2014) 1209–1219.

[30] A.A. Gouda, A.S. Amin, Cloud-point extraction, preconcentration and spectrophotometric determination of trace quantities of copper in food, water and biological samples, Spectrochim. Acta Part A Mol. Biomol. Spectrosc., 120 (2014) 88–96.

[31] Y. Yamini. M. Faraji, S. Shariati, R. Hassani, M. Ghambarian, On-line metals preconcentration and simultaneous determination using cloud point extraction and inductively coupled plasma optical emission spectrometry in water samples, Anal. Chim. Acta, 612 (2008) 144–151.

[32] H. Bektas, Ş. Ceylan, N. Demirbas, Ş. Alpay-Karaoğlu, B.B. Sökmen, Antimicrobial and antiurease activities of newly synthesized morpholine derivatives containing an azole nucleus, Med. Chem. Res., 22 (2013) 3629–3639.

[33] C. Duran, D. Ozdes, D. Sahin, V.N. Bulut, A. Gundogdu, M. Soylak, Preconcentration of Cd(II) and Cu(II) ions by coprecipitation without any carrier element in some food and water samples, Microchem. J., 98 (2011) 317–322.

[34] L. Kocúrová, I.S. Balogh, V. Andruch, Dispersive liquid-phase microextraction procedure for spectrometric determination of cadmium, Microchem. J., 107 (2013) 3–9.

[35] N. Altunay, R. Gürkan, A new cloud point extraction procedure for determination of in organic antimony species in beverages and biological samples by flame atomic absorption spectrometry, Food Chem., 175 (2015) 507–517.

[36] H.İ. Ulusoy, R. Gürkan, Ü. Aksoy, M. Akçay, Development of a cloud point extraction and preconcentration method for determination of trace aluminum in mineral waters by FAAS, Microchem. J., 99 (2011) 76–81.

[37] M. Khan, T.G. Kazi, H.I. Afridi, M. Bilal, A. Akhtar, N. Ullah, S. Khan, S. Talpur, Application of ultrasonically modified cloud point extraction method for simultaneous enrichment of cadmium and lead in sera of different types of gallstone patients, Ultrason. Sonochem., 39 (2017) 313–320.

[38] M. Bilal, T.G. Kazi, H.I. Afridi, M.B Arain, J.A. Baig, M. Khan, N. Khan, Application of conventional and modified cloud point extraction for simultaneous enrichment of cadmium, lead and copper in lake water and fish muscles, J. Ind. Eng. Chem., 40 (2016) 137–144.

[39] N. Jalbani, M. Soylak, Preconcentration/separation of lead at trace level from water samples by mixed micelle cloud point extraction, J. Ind. Eng. Chem., 29 (2015) 48–51.

[40] D. Citak, M. Tuzen, A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry, Food Chem Toxicol., 48 (2010) 1399–1404.

[41] J.L. Manzoori, A. Bavili-Tabrizi, Cloud point preconcentration and flame atomic absorption spectrometric determination of Cd and Pb in human hair, Anal. Chim Acta, 470 (2002) 215–221.

[42] Naeemullah, T. Gul Kazi, M. Tuzen, Development of novel simultaneous single step and multistep cloud point extraction method for silver, cadmium and nickel in water samples, J. Ind. Eng. Chem., 35 (2016) 93–98.

[43] E.L. Silva, P.S. Roldan, Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry, J. Hazard. Mater., 161 (2009) 142–147.

[44] N. Dallali, M.M. Zahedi, Y. Yamini, Simultaneous cloud point extraction and determination of Zn Co, Ni and Pb by flame atomic absorption spectrometry, using 2 guanidinobenzimidazole as the complexing agent, Sci. Iran, 14 (2007) 291–296.

[45] S. Candir, I. Narin, M. Soylak, Ligandless cloud point extraction of Cr(III), Pb(II), Cu(II), Ni(II), Bi(III), and Cd(II) ions in environmental samples with Tween 80 and flame atomic absorption spectrometric determination, Talanta, 77 (2008) 289–293.

Supplementary

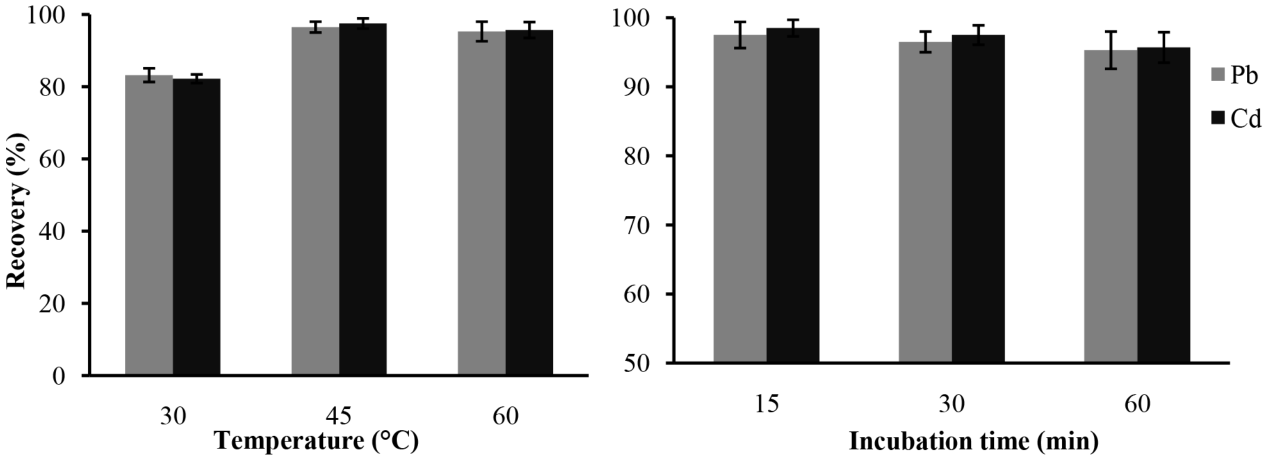

Fig. S1. Effect of equilibrium temperature (A) and Incubation time (B) on the recovery of Cd(II) and Pb(II) ions. Extraction conditions: 50 mL aqueous standard volume, pH = 8.0, TX-114 conc.: 0.2 % (w/v), MPAPTAH amount: 0.70 mg, centrifugation time of 5 min; centrifugation rate of 2000 rpm. (n = 3).

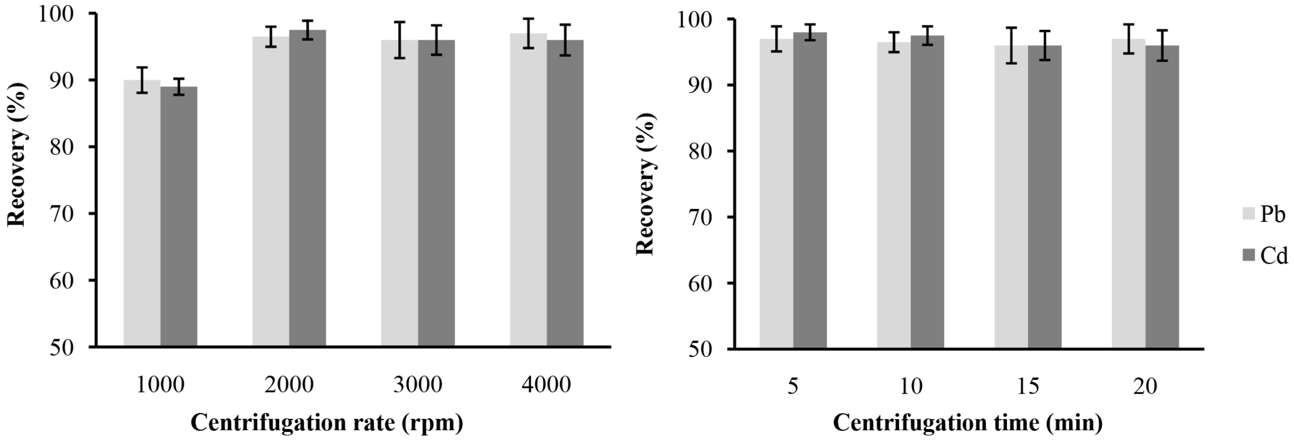

Fig. S2. Effect of centrifugation rate (A) and time (B) on the extraction of Cd(II) and Pb(II) ions. Extraction conditions: 50 mL aqueous standard volume, pH = 8.0, TX-114 conc.: 0.2 % (w/v), MPAPTAH amount: 0.70 mg, equilibrium temperature 45°C; equilibrium time of 15 min. (n = 3).