Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc. *84* (4) 435–443 (2019)
JSCS–5196

UDC 546.48–71+543.391.34:547.295.71'262+
546.212:502/504
Short communication

SHORT COMMUNICATION

Undecanol–ethanol–water ternary system-based microextraction for the detection of cadmium

OYA AYDIN URUCU[1]*, ECE KOK YETIMOGLU[1], SEYDA DONMEZ[1]
and SABAHATTIN DENIZ[2]

[1]Marmara University, Faculty of Science and Letters, Chemistry Department, Goztepe Campus, 34722, Istanbul, Turkey and [2]Marmara University, Faculty of Technology, Textile Engineering Department, Goztepe Campus, 34722, Istanbul, Turkey

(Received 31 August, Revised 9 November, accepted 13 December 2018)

Abstract: An eco-friendly, simple, and sensitive solidification of floating organic drop based dispersive liquid–liquid microextraction (SFODME) procedure was introduced for the separation and preconcentration of cadmium. After 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) was complexed with cadmium ions in sample, the undecanol–ethanol–water ternary system was used as an organic solvent for extraction. The main factors relevant to the microextraction efficiency such as pH, concentration of 5-Br-PADAP, amount of extraction solvent were optimized. The detection limit is 0.01 μg L^{-1} along with preconcentration factor 266. The recovery of the analyte was between 98 % and 103 %, with relative standard deviation below 6 %. The developed procedure was successfully tested on the analysis of water, hair dye, and food samples.

Keywords: eco-friendly; GFAAS; microextraction; heavy metal ions.

INTRODUCTION

Cadmium is a heavy metal that is widely found in the earth's crust and is often used for industrial activities.[1] The increased use of cadmium in industrial activities within the last century resulted in increased contamination in environmental samples and thus raised the human exposure. Cadmium is mostly found in water, food and cigarette smoke as a contaminant. It can cause kidney, lung and liver diseases as well as high blood pressure, nerve and brain damage by directly affecting the DNA or by damaging the DNA repair mechanisms. For this reason, many methods have been developed with the purpose of analysis and removal of cadmium from matrices in water and food samples.[1,2]

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*Corresponding author. E-mail: oaydinurucu@gmail.com

https://doi.org/10.2298/JSC180831110U

Graphite furnace atomic absorption spectrometry (GFAAS) is one of the instrumental techniques used in the determination of cadmium in different samples due to its good sensitivity, speed and accuracy while compared to other analytical techniques (*e.g.*, FAAS, UV–Vis spectrophotometry).[3,4] Water and food samples have both very low cadmium levels and have matrix effects. For these reasons, the direct detection of cadmium is very difficult and generally separation, preconcentration method is necessary. Several methods such as liquid-liquid extraction (LLE), solid phase extraction (SPE) have been used for the separation- preconcentration of cadmium ions. These methods require large volume of sample and high amount of organic solvent. In recent years, several preconcentration methods have been developed based on green chemistry principles such as cloud point extraction (CPE),[5] single-drop microextraction (SDME),[6] solid phase microextraction (SPME), dispersive liquid–liquid microextraction (DLLME),[7,8] supramolecular solvent extraction (SsE)[9] and solidified floating organic drop microextraction (SFODME).[10,11] These techniques reduce organic and acid solution consumption, thus reducing the amount of hazardous waste. In addition, they reduce cost and analysis time.[12] The SFODM technique also has advantages such as high enrichment factor, and operation simplicity. Determination of Cd (II) ions in various samples are carried out with many complexing agents such as dithizon, 4-(2-pyridylazo)-resorcinol,5,7-dibromo-8-hydroxyquinoline, pyruvylidine-2--hydrazinobenzothiozole and rhodamine 6G. However, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) has more sensitivity and selectivity for determination of Cd (II) ions by spectrophotometric method.[13] In a lot of studies 5-Br-PADAP was used as complexing agent for the enrichment–separation of trace amounts of Cd (II) ions.[7,14,15] In our literature survey, 5-Br--PADAP-Cd (II) complex was not used for preconcentration of Cd (II) ions in various samples by SFODME.

In this study, we used water + 1-undecanol + ethanol ternary system as an extraction system. This system is faster than other DLLME procedures.[16] We also used 5-Br-PADAP as a chelating reagent. We combined SFODME method with graphite furnace atomic absorption spectrometer (GFAAS) for separation, enrichment and determination of cadmium in different samples. We tested our method with water, hair dye and food samples.

EXPERIMENTAL

Instrumentation

Mettler Toledo pH meter was used to measure the pH. A Precisa XB 220A model precision scale was used for mass measurements and Hettich EBA 21 model centrifuge was used for centrifugation. An AAS ZEEnit 700P atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with deuterium background correction, equipped with a transversely heated graphite tube atomizer, was used for all measurements. The temperature program for the ETAAS is shown in Table I. The cadmium hollow cathode lamp (Analytic Jena AG, Konrad, Zuse, Germany) was operated at 4.0 mA and analytical line at 228.8 nm was used with a spectral bandwidth of 0.5 nm. Anton Paar Multiwave 3000 microwave digestion system was used for sample digestion.

TABLE I. The temperature program of graphite furnace atomizer

Step	Start temperature, °C	Ramp time, s	Hold time, s
Drying	110	5	10
Pyrolysis	500	20	10
Atomizing	1900	0	5
Cleaning	2200	0	4

Reagents and solutions

All solutions were prepared with analytical grade reagents and double deionised water. All glassware in the experiments were soaked in 10 % HNO_3 solution for one day and cleaned with double distillate water. 1000 mg L^{-1} of stock standard solution for Cd was obtained from Merck. 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) used as a complexing agent and was prepared by dissolving an appropriate amount of 5-Br-PADAP (Sigma-Aldrich) in ethanol. 1-Undecanol was used as an extracting solvent (Merck). KH_2PO_4/Na_2HPO_4 buffer solutions were used to adjust the pH.

Preparation of samples

The proposed procedure was applied to food, hair dye and water samples to validate for cadmium ions detection. Biscuit, which was used as a food sample and hair dye were purchased from local market. Microwave assisted acid digestion method was used for digestion of biscuit and hair dye samples. 0.2 g of the sample were transferred into the microwave vessels and then 5 mL HNO_3, 3 mL H_2O_2 (30 %) were added. Optimized microwave program (240 °C for 20 min) was applied. The water samples (tap water, rain water and river water) were collected in Turkey. All samples were filtered through a 0.45 pore size membrane filter and stored in polyethylene bottles at 4 °C in the dark.

Extraction procedure

Aliquots of 10 mL standard solution containing 5 μg L^{-1} Cd were adjusted to pH 8 with a KH_2PO_4/Na_2HPO_4 buffer solution in a 15 mL conical centrifuge tube while ionic strength was set to 2 % by using NaCl. The amounts of 1mL 5-Br-PADAP (2.86×10^{-3} mol L^{-1}) in ethanol and 75 μL 1-undecanol were quickly injected into the sample solution by using a syringe. The mixture was centrifuged for 10 min at 5000 rpm and fine droplets of 1-undecanol floated on the surface of the aqueous solution, because, 1-undecanol has lower density than water. After cooling the sample tube in an ice bath the organic solvent was solidified and adhered to the inner surface of the tube, the water phase was taken up with a pipette and the organic phase diluted to 300 μL with ethanol. The solution was then analysed by using the GFAAS (Fig. 1).

RESULTS AND DISCUSSION

Optimization procedure variables

In this procedure, we combined SFODME method with GFAAS for the detection of cadmium in various samples. Various important parameters such as pH, 5-Br-PADAP concentration, amount of 1-undecanol and salt effect were studied and optimized to obtain high enrichment factors.

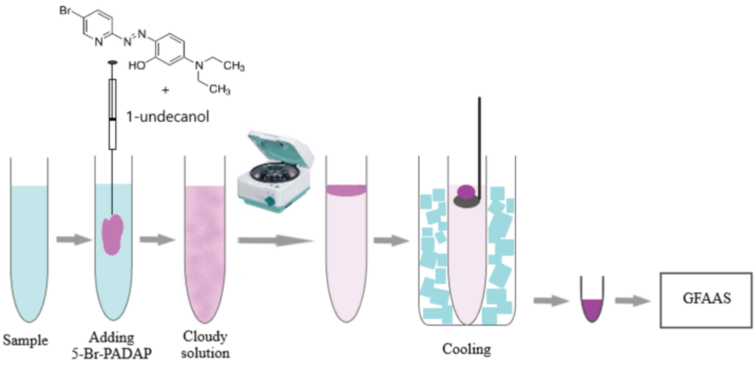

Fig. 1. Sematic diagram of SFODME procedure.

Selection of the extraction solvent is critical in SFODME method in order to achieve high recovery and enrichment factor. The extraction solution should have low toxicity, low water solubility, low volatility, melting point (m.p.) close to room temperature (10–30 °C), and should not interfere with analytical techniques used to determine the analytes. Thus, 1-undecanol (m.p. 13–15 °C), 1-dodecanol (m.p. 24–27 °C) were assayed as the extraction solvent. The extraction efficiency was found to be higher with 1-undecanol than with 1-dodecanol, so 1-undecanol was chosen as an extraction solvent. The influence of 1-undecanol volume on the absorption of Cd (II) in the SFODME was also examined in the range 25–150 μL with keeping other analytical parameters constant. The result shows that the analytical signal gradually increases as the volume of the floating phase increases by about 35 to 80 μL. When the volume of 1-undecanol was above 80 μL, the analytical signal began to decrease. The result is that the enrichment factor decreases with increasing 1-undecanol volume; by the increase of the volume of 1-undecanol, the volume of the floating phase rises. However, due to the dilution effect, the increase in the volume of the extraction solvent caused a slight decrease in the analytical signal.[17,18] Since the optimum analytical signal was obtained using 75 μL 1-undecanol volume, it was selected for the following experiments (Fig. 2).

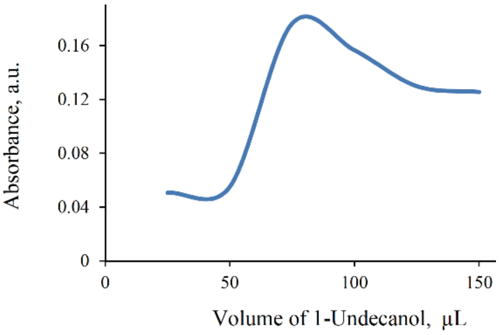

Fig. 2. The influence of extraction solvent volume on adsorption of cadmium. Concetration of Cd: 5μg L^{-1}; pH 8; sample volume 10 mL; content of NaCl: 2 %; concentration of [5-Br-PADAP]: 2.86×10^{-4} mol L^{-1}.

The separation of metal ions by SFODME requires the preformation of a complex to be extracted into the small extraction volume. pH plays an important role in the metal–chelate formation and the extraction procedures. Alkaline pH values are favourable for complexation of cadmium and 5-Br-PADAP.[19] The influences of pH on the absorbance at a constant concentration of a complex in 1-undecanol were studied in the range of 6–9. The results are shown in Fig. 3. The highest absorbance for the detection of Cd (II) was obtained in pH 8. Therefore, all the following studies were achieved at pH 8.

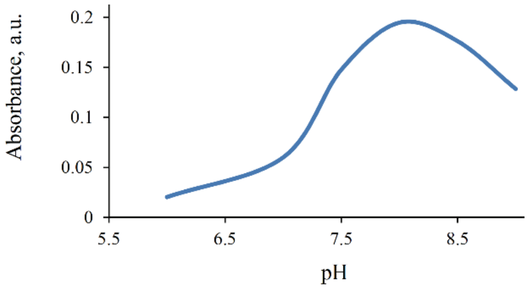

Fig. 3. The influence of pH on adsorption of cadmium. Concetration of Cd: 5 μg L^{-1}; volume of 1-undecanol: 75 μL; sample volume 10 mL; content of NaCl: 2 %; concentration of 5-Br-PADAP: 2.86×10^{-4} mol L^{-1}.

The Cd (II) forms a coloured complex with 5-Br-PADAP. The mole ratio between Cd (II) and 5-Br-PADAP is 1:2 in complex.[19] Fig. 4. portrays the concentration effect of 5-Br-PADAP on analytical response. As seen in Fig. 4, the intensity of the absorbance reached a maximum when the concentration of 5-Br-PADAP was 2.86×10^{-4} was mol L^{-1}. The maximum absorbance is attributed to the complete extraction of Cd analyte. Therefore, for the further experiments, the concentration of 2.86×10^{-4} mol L^{-1} for 5-Br-PADAP was chosen as the optimal one.

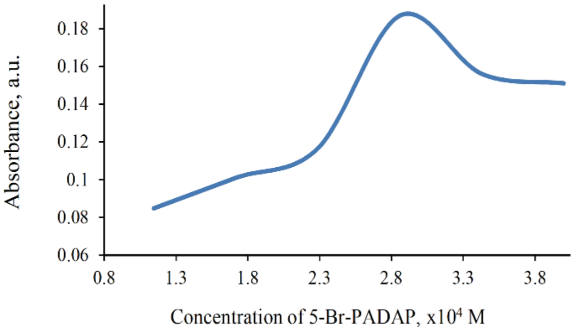

Fig. 4. The influence of 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol concentration on adsorption of cadmium. Concentration of Cd 5μg L^{-1}; pH 8; volume of 1-undecanol: 75 μL; sample volume 10 mL; content of NaCl: 2 %.

Generally, the ionic strength increases with the raise of salt concentration, whereas the aqueous solubility of the analyte decreases. This salting-out effect causes the analytes to migrate more easily from the sample to the organic phase, thus the salt addition improves the extraction efficiency and sensitivity,[20] that's why the effect of salt concentration on the newly developed extraction procedure has been investigated. The appropriate concentration was found to be 2 % as seen in Fig. 5.

Effects of common ions

The effect of different metal ions on the analytical signal in the preconcentration procedure was investigated. The solutions were prepared containing 5 μg L^{-1} Cd and various numbers of foreign ions and then SFODME procedure was applied as described previously. The concentrations of added species produce less than ±5 % relative error in absorbance readings. The results are shown in Table II.

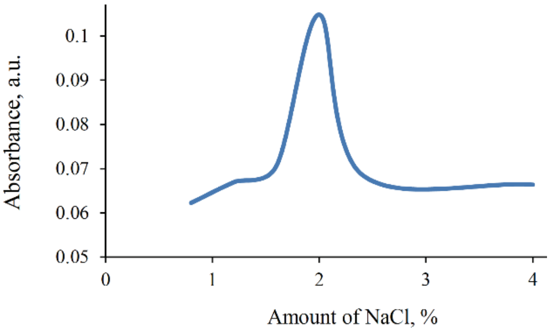

Fig. 5. The influence of the amount of salt on adsorption of cadmium. Concentration of Cd: 5μg L^{-1}; volume of 1-undecanol: 75 μL; pH 8; sample volume 10 mL; concentration of 5-Br-PADAP: 2.86×10^{-4} mol L^{-1}.

TABLE II. Effect of the coexisting ions on the recoveries of the cadmium ions

Coexisting ion	Mole ratio, ion/Cd^{+2}	Recovery, %
Ba^{+2}	2000	99.3±1.1
K^{+}	2000	102.6±2.1
Pb^{+2}	1000	98.7±1.8
Ni^{+2}	800	98.1±2.2
Cu^{+2}	700	98.4±1.5
Ag^{+}	300	99.2±0.9
Zn^{+2}	300	101.0±1.9
Mg^{+2}	300	99.7±1.7
Hg^{+2}	300	98.2±2.3
Co^{+2}	300	99.5±2.4
Fe^{+3}	200	100.2±0.7

Effect of sample volume

The effects of sample volume on the recovery of Cd (II) ions were investigated in the volumes from 10 to 100 mL, using the model solutions prepared in optimal conditions. Quantitative recovery was obtained for up to 80 mL. The preconcentration factor for Cd (II) was calculated by taking the ratio of the highest sample volume (80 mL) and the lowest final volume (0.3 mL) and was 266.

Method validation and application to real samples

The accuracy of the recommended SFODME procedure was firstly tested by the method of standard addition. Hence various amounts of cadmium ions were spiked in river water and tap water, and then Cd(II) concentrations were detected by the developed procedure. Also, biscuit and hair dye sample contents were detected by the developed procedure and the results were for the compared certified values of Cd (II) content. Results and recoveries are shown in Tables III and IV. The certified reference material SSWW2 was also analysed by the developed method for Cd (II) ions. The results are good agreement with the certified value (Table III).

TABLE III. Determination of cadmium ions in water samples; n. d. – not detected

Sample	Added amount of Cd^{2+}, μg L^{-1}	Found amount of Cd^{2+}, μg L^{-1}	Recovery, %
Tap water	0	n. d.	n. d.
	10	9.754	98±0.2
	20	19.12	96±0.2
	25	24.78	99±0.1
River water	0	n. d.	n. d.
	10	10.32	103±0.01
	20	20.62	103±0.02
	25	24.34	97±0.1

TABLE IV. Determination of cadmium ions in water, hair dye and biscuit samples

Sample	Certified amount of Cd^{2+}, μg L^{-1}	Found amount of Cd^{2+}, μg L^{-1}
SPSWW2	100±0.5	100.14±0.05
Biscuit	12±0.2	12.42±0.05
Hair dye	0.05±0.002	0.047±0.002

Analytical performance of the method

The analytical parameters were obtained for the detection of cadmium under the optimum condition (Table V). The calibration graph was linear in the range

TABLE V. Comparison of the SFODM method with some recent studies on separation and preconcentration of Cd (II) ions reported in literature; CPE: cloud point extraction; SPE: solid phase extraction; SFODME: solidified floating organic drop microextraction; GFAAS: graphite furnace atomic absorption spectrometry; FAAS: flame atomic absorption spectrometry; UV-Vis: ultraviole visible; LOD: limit of detection; E.F: enrichment factor; P.F: preconcentration factor; R: Reference

Technique	Sample	E.F/P.F	*LOD* μg L^{-1}	Concentration linear range, μg L^{-1}	Ref.
CPE-FAAS	Water and food samples	20	0.21	10–500	21
Coprepitation–FAAS	Real liquid/solid samples	50	0.2	–	22
SPE–UV–Vis	Plant and biological samples	–	0.8	–	23
SFODME–FAAS	Water samples	63	0.57	2.0 – 400	24
SFODME–UV–Vis	Saffron samples	–	0.5	1–500	25
SFODME–FI-AAS	Water samples	640	0.0079	0.08 – 30	26
SFODME–GFAAS	Water, hair dye and food samples	266	0.012	0.04–30	This study

of 0.04-305 μg L^{-1} of Cd (II), with a correlation coefficient (R^2) of 0.993. The preconcentration factor was 266, calculated from the ratio of phase volumes. The limit of detection (*LOD*) of the developed method was defined as 3*Sb*/*m* (*Sb*: standard deviation of the blank ($n = 8$), *m*: the slope of the calibration graph) and was found to be 0.012 μg L^{-1}. The relative standard deviations (*RSD*) for eight repeated measurements of 5 μg L^{-1} of Cd were 2.1 %.

CONCLUSION

The proposed method gives a highly sensitive, simple, environmentally friendly, and low-cost technique for GFAAS detection of the trace amount of cadmium ion in various samples. An effective water + 1-undecanol + ethanol ternary system was used for extraction. The procedure has both lower detection limit and good *R.S.D.* The analytical performance of this method is comparable with previous methods for the detection of cadmium. Table V indicates that this novel method is a good alternative for the accurate and the precise detection of cadmium in food and water samples.

Acknowledgement. This study is supported by Marmara University, Scientific Research Commission of Turkey (Project No: FEN-A-131016-0465).

ИЗВОД

МИКРОЕКСТРАКЦИЈА ЗАСНОВАНА НА ТЕРНАРНОМ СИСТЕМУ УНДЕКАНОЛ–ЕТАНОЛ–ВОДА ЗА ДЕТЕКЦИЈУ КАДМИЈУМА

OYA AYDIN URUCU[1], ECE KOK YETIMOGLU[1], SEYDA DONMEZ[1] и SABAHATTIN DENIZ[2]

[1]Marmara University, Faculty of Science and Letters, Chemistry Department, Goztepe Campus, 34722, Istanbul, Turkey и *[2]Marmara University, Faculty of Technology, Textile Engineering Department, Goztepe Campus, 34722, Istanbul, Turkey*

Представљена је еколошки прихватљива, једноставна и осетљива дисперзивна течно-течно микроекстракција заснована на солидификацији лебдеће органске капљице (SFODME) за сепарацију и преконцентрацију кадмијума. Након што је 2-(5-бромо-2пиридилазо)-5-(диетиламино)фенол (5-Br-PADAP) комплексиран са кадмијумовим јонима, употребљен је систем ундеканол–етанол–вода као органски растварач за екстракцију. Оптимизовани су главни фактори релевантни за ефикасност микроекстракције, као што је pH, концентрација 5-Br-PADAP, количина екстракционог растварача. Граница детекције је 0,01 μg L^{-1}, са фактором преконцентрације 266. Принос аналита је био између 98 и 103 %, са релативном стандардном девијацијом испод 6 %. Развијени поступак је успешно тестиран у анализама воде, боје за косу и хране.

(Примљено 31. август, ревидирано 9. новембар, прихваћено 13. децембра 2018)

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