Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.868838

53 (2015) 2686–2691
March

Taylor & Francis
Taylor & Francis Group

Ultrasonication ionic liquid-based dispersive liquid–liquid microextraction of palladium in water samples and determination of microsampler system-assisted FAAS

Demirhan Citak*, Mustafa Tuzen

Faculty of Science and Arts, Chemistry Department, Gaziosmanpaşa University, Tokat 60250, Turkey
Tel. +90 356 2521616; Fax: +90 356 2521585; email: demirhan.citak@gop.edu.tr

Received 12 July 2013; Accepted 15 November 2013

ABSTRACT

In the proposed approach, a simple and efficient ultrasonication ionic liquid-based dispersive liquid–liquid microextraction (UIL-DLLME) was described. Microsampler system-assisted flame atomic absorption spectrometer was used at the determination step of Pd(II). 1-Phenylthiosemicarbazide (PTC) and 1-hexyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide [C_6mim][Tf_2N] were used as the chelating agent and the extraction solvent of UIL-DLLME, respectively. Ultrasonication was used for dispersing of [C_6mim][TF_2N] into samples. Different experimental conditions affecting UIL-DLLME of Pd(II) were examined and optimized. The analytical performance characteristics of investigated method including limit of quantification (33 $\mu g\,L^{-1}$), limit of detection (11 $\mu g\,L^{-1}$), relative standard deviation (% 3.1), linear range (33–500 $\mu g\,L^{-1}$), and enrichment factor (52) were calculated. The optimized UIL-DLLME was applied to different water samples.

Keywords: Ionic liquid; Ultrasonication; Microextraction; Microsampler system; Flame atomic absorption spectrometry

1. Introduction

Palladium has economic importance because of its extensive use in various metallurgical industries, chemical synthesis, manufacture of medical devices, and jewelry. However, there is no role of palladium in any biological processes and all palladium compounds are known to be highly toxic and carcinogenic [1–3]. Due to its economical and environmental importance, there is a necessity to determine trace concentration of palladium in environmental samples by highly sensitive analytical techniques, such as flame atomic absorption spectrometry (FAAS) [4–6], graphite furnace atomic absorption spectrometry [7,8], high-performance liquid chromatography [9], inductively coupled plasma atomic emission spectrometry (ICP-OES) [10–12], and inductively coupled plasma mass spectrometry [13].

Despite highly sensitive analytical techniques, direct determination of trace analytes is often problematic in complex matrix and low concentrations for analytes [14–17]. As a result, a separation and preconcentration step is needed prior to trace palladium analysis. DLLME is an excellent and the

---

*Corresponding author.

most frequently used liquid–liquid extraction technique among the conventional separation and preconcentration methods [18–20]. Halogenated organic reagents, such as chlorobenzene, carbon disulfide, chloroform, and carbon tetrachloride, are usually used as extraction solvents and ethanol, methanol, acetonitrile, or acetone are usually used as disperser solvents in microextraction processes [21–24]. Nowadays, ILs are often used as extraction solvents instead of traditional organic solvents in DLLME methods. Some of the physical and chemical properties of ILs, which make them attractive for extraction processes, are nonflammable nature, negligible vapor pressure, lower reactivity, and high density. They are ecological friendly solvents [25–28]. It is a known fact that ultrasonication is a powerful technique in the processes of separation and extraction. When it is applied, it causes emulsion, homogenizing, and mass transferring between immiscible phases [29].

As a result, we have developed a new and green ultrasonication ionic liquid-based dispersive liquid–liquid microextraction (UIL-DLLME) methodology for the enrichment of Pd(II). The formation of a cloudy extraction mixture was obtained by ultrasonication. The levels of Pd(II) in environmental samples were determined by microsampler system-assisted flame atomic absorption spectrometer.

2. Experimental

2.1. Apparatus, reagents, and chemicals

The concentrations of Pd(II) were measured by using a flame atomic absorption spectrometer (Perkin–Elmer Analyst 700 with deuterium background corrector). Microsample introduction system, which was adapted to FAAS, was made by technological systems [30]. A Sartorius pp-15 Model pH meter, a Nuve model NF 800 centrifuge, and a Bandelin Sonorex RK 512 CH (35 kHz) ultrasonic bath were used during the optimization steps of UIL-DLLME.

All chemicals used in the experiment were of analytical reagent grade. 1-Phenylthiosemicarbazide (PTC) and 1-hexyl-3-methyl imidazolium bis(trifluoro methylsulfonyl)imide ([C_6mim][Tf_2N]) were obtained from the chemical company Merck (Germany). All dilutions for working solutions were made daily by using double-distilled deionized water.

2.2. Optimization of microsampler system

To achieve an optimal injection volume, an extraction solvent (50–300 μL) containing of 2.5 mg L^{-1} of Pd (II) was introduced to the microsampler system. The recoveries of Pd(II) were used for evaluating tests. The recoveries were quantitative (≥95%) in the range of 100–300 μL.

2.3. General procedure

A 9-ml buffered solution (pH 5.0) containing 50 μg L^{-1} Pd(II), 1 mg PTC, and 150 μL [C_6mim][Tf_2N] was placed in a 15-mL centrifuge tube. The mixture was vortexed for 1 min and immediately removed to ultrasonic bath for 10 min. The extractant ([C_6mim][Tf_2N]) was dispersed into solution and cloudy solution was formed. Then, the hydrophobic complex of Pd(II) was extracted into droplets of [C_6mim][Tf_2N]. The cloudy solution was centrifuged at 4,000 rpm for 5 min. Droplets of [C_6mim][Tf_2N] were sedimented at the bottom of the centrifuge tube (about 120 μL). About 120 μL of the sediment phase was taken by 250 μL microsyringe. To reduce viscosity, the last volume of the extractant was set to 200 μL with ethanol and injected into the microsampler-assisted FAAS.

2.4. Pretreatment of Pd(II) in water samples

The water samples were acidified with nitric acid after collection and filtered for any particles. The proposed UIL-DLLME was applied to sea water (Blacksea, Ordu), river water (Yeşilırmak, Tokat), lake water (Almus, Tokat), and tap water (Taşlıçiftlik, Tokat).

3. Results and discussion

3.1. Effect of [C_6mim][Tf_2N] volume

During the UIL-DLLME processes, volume of IL is a critical factor which could obviously influence the extraction performance [31]. In order to test the effect of [C_6mim][Tf_2N] on the extraction performance, volumes of extractant ranging from 100 to 300 μL were subjected to the improved procedure. The volume of the final [C_6mim][Tf_2N] phase was diluted with ethanol for reducing viscosity before analysis. As seen from Fig. 1, quantitative recoveries of Pd(II) ($R \geq 95\%$) were obtained by adding 150 μL volume of [C_6mim][Tf_2N]. Thereby, the volume of 150 μL was applied to recover the analyte from samples.

3.2. Effect of ultrasonication and centrifugation time

In this work, the ultrasonication time plays an important role in the formation of a cloudy mixture, and this factor affects the extraction efficiency of UIL-

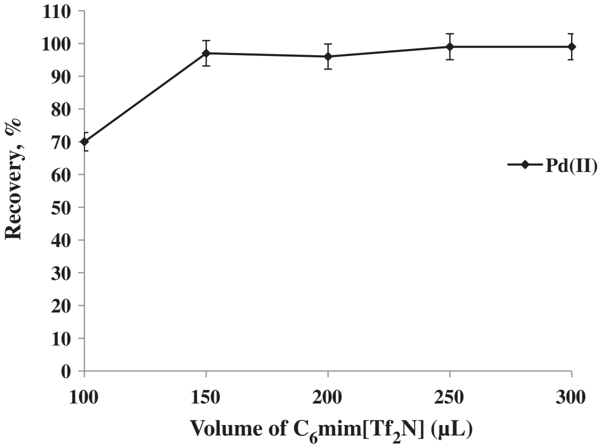

Fig. 1. Effect of $[C_6mim][Tf_2N]$ volume (N = 3).

DLLME. For a reliable quantitation of Pd(II) ultrasonication time was investigated in the range 0–20 min (Fig. 2). It was seen that a cloudy mixture was formed after 6 min. But, the recoveries of Pd(II) were not quantitative. When the ultrasonication time was longer than 10 min, the recoveries of Pd(II) were quantitative. Herein, ultrasonication time of 10 min was found to be an optimal condition for extraction procedure. To optimize centrifugation conditions, centrifugation rate (1,000–4,500 rpm) and time (1.0–10 min) were also tested. It was found that 4,000 rpm for 5 min was enough for quantitative extraction efficiency.

3.3. Effect of pH

The performance of UIL-DLLME process is also related with the formation of hydrophobic complex and stability of complex [32,33]. The pH of the solution system plays an important role in this step. In order to obtain the quantitative extraction, the effect of pH was investigated in the pH range of 2.0–7.0. As can be seen in Fig. 3, the recovery of Pd(II) increased in the range of 2.0–5.0 and then decreased with the increase of pH value. Thus, a value of pH 5.0 was selected for subsequent work.

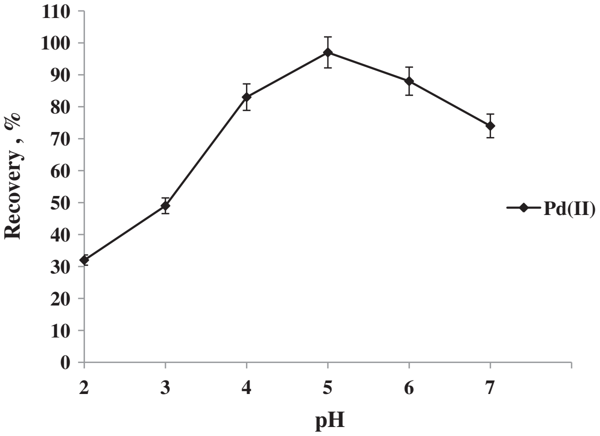

Fig. 3. Effect of pH (N = 3).

3.4. Effect of the PTC concentration

The amount of complexing agent is a significant parameter that has been found to affect the extraction performance in preconcentration methods. 1-Phenylthiosemicarbazide was selected to form Pd-PTC complex. The effects of the PTC amount on UIL-DLLME were studied in the range of 0.0–1.5 mL of PTC (1%, w/v). The stock solution of PTC was daily prepared. The results were illustrated in Fig. 4. It was found that the recovery of Pd(II) increased with the increasing of PTC amount, and then remained constant at 1.0 mL of 0.1% PTC. Therefore, 1 mL of PTC (1 mg) amount was chosen for further experiments.

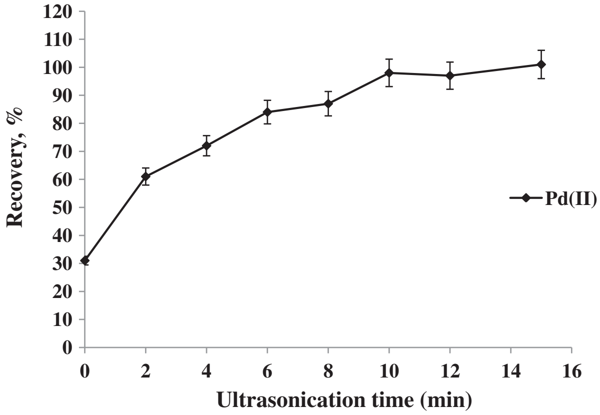

Fig. 2. Effect of ultrasonication time.

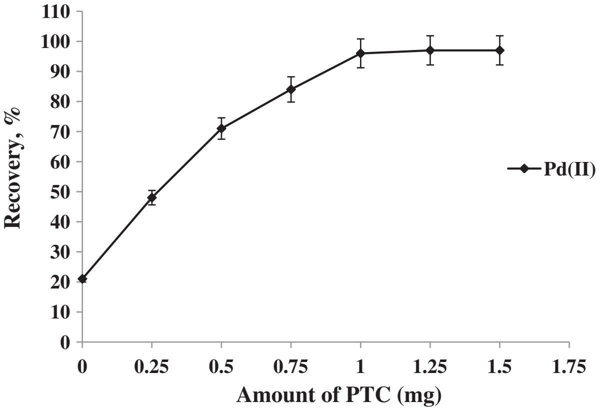

Fig. 4. Effect of complexing agent on UIL-DLLME of Pd(II) (N = 3).

Table 1
Effect of some matrix ions on microextraction of Pd(II), (*N* = 3)

Ion	Interference/metal ratio	Pd(II) recovery, %
Na^+	1,000	98 ± 3*
K^+	850	97 ± 2
Ca^{2+}	500	99 ± 2
Mg^{2+}	500	101 ± 2
Cl^-	3,500	97 ± 2
NO_3^-	2,500	97 ± 3
SO_4^{2-}	2000	99 ± 2
PO_4^{3-}	2,500	98 ± 3
Zn^{2+}	50	104 ± 4
Fe^{3+}	50	96 ± 2
Mn^{2+}	50	97 ± 2
Al^{3+}	50	96 ± 2

*Mean ± standard deviations.

3.5. Effect of coexisting ions

To evaluate the applicability of designed methodology, the effect of common matrix ions in water samples on separation and determination of target Pd (II) was investigated. Under selected UIL-DLLME conditions (pH 5, 1 mg PTC and 150 μL, 10 min ultrasonication time), model solutions of 50 μg L^{-1} Pd (II) containing the added matrix ions were applied according to developed procedure. The tolerance limits of the matrix ions were defined as in the range of 95–105%. As it could be seen from Table 1, the presence of matrix ions in the various water samples has no significant effect on selective and effective UIL-DLLME of Pd(II).

3.6. Accuracy and application of UIL-DLLME

The combination of UIL-DLLME and microsampler system-assisted FAAS was applied for the determination of Pd(II) in sea water (Blacksea, Ordu), river water (Yeşilırmak, Tokat), lake water (Almus, Tokat), and tap water (Taşlıçiftlik, Tokat). In order to validate the accuracy of the proposed procedure, the recovery experiments were carried out. Sample volumes of 9.0 mL containing known masses of Pd(II) were buffered at pH 5. The procedure in section 2.3 was applied to the solutions. The results are tabulated in Table 2. The achieved recoveries (95–99%) were confirming the accuracy of the UIL-DLLME and indicating that the developed UIL-DLLME method can be applied to water samples for the determination of Pd(II).

Table 2
Analytical results for determination of Pd(II) in water samples (sample volume: 9 mL, final volume: 200 μL (*N* = 4))

		Sea water		River water		Lake water		Tap water	
Element	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)
Pd	0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	50	48 ± 3*	96	49.1 ± 2.8	98	47.5 ± 3.6	95	49.5 ± 2.0	99
	100	95 ± 4	95	96.7 ± 5.3	97	98.2 ± 3.5	98	97.3 ± 4.1	97

*Mean ± standard deviation, BDL: below detection limit.

Table 3
Comparison of presented UIL-DLLME with published preconcentration methods

Preconcentration/determination technique	EF	pH	DL (μg L^{-1})	RSD (%)	References
CPE/ICP-OES	20.2	6.5	0.3	3.8	[11]
SFODME based on USD/FAAS	49.9	2.0	0.60	2	[34]
DLLME/FAAS	45.7	–	90	0.7	[35]
Co-precipitation/FAAS	25	4.0	2.1	<10	[36]
SPE/FAAS	60	7.0	1.5	2.4	[37]
M-CIAME/spectrophotometry	97	4.0	0.2	1.7	[38]
UIL-DLLME	52	5.0	11	3.1	This work

SFODME based on USD: Solidified floating organic drop microextraction based on ultrasound-dispersion. M-CIAME: Modified cold-induced aggregation microextraction. CPE: Cloud point extraction. SPE: Solid phase extraction.

3.7. Evaluation of method performance of analytical processes

Performance characteristics of analytical optimized process, such as limit of detection (LOD), reproducibility, linear range, calibration graph, and preconcentration factor, were evaluated under optimal experimental conditions. The calibration curve was linear in the range of 33–500 $\mu g\,L^{-1}$ of Pd(II). The LOD, defined as three times the standard deviations of the blank (N: 11), was 11 $\mu g\,L^{-1}$. The relative standard deviation (RSD) for 11 replicate measurements of 50 $\mu g\,L^{-1}$ Pd(II) was 3.1%. The preconcentration factor was 45 and it was calculated by the ratio of the highest sample volume (9.0 mL) and the lowest final volume (200 μL). The enrichment factor (EF), calculated as the ratios of the Pd(II) concentration in the IL-rich phase to initial water phase, was 52.

Some characteristic data of the reported works for UIL-DLLME, like pH, enrichment factor, RSD, and LOD, are summarized in Table 3 for comparison. As can be seen from Table 3, it has high enrichment factor, low LOD, and RSD for the analysis of Pd(II) in water samples.

4. Conclusions

A new and efficient method of UIL-DLLME coupled with microsampler system-assisted FAAS was described for the enrichment and determination of Pd (II) in water samples. Dispersion of extraction solvent was achieved by ultrasonication. Extraction of Pd-PTC complex was readily provided by this way and without using a dispersion solvent. This improved technique also has many advantages, such as simplicity of operation, short extraction time, good accuracy and precision, low cost, high enrichment factor, and minimum organic solvent consumption.

Acknowledgement

The authors are grateful for the financial support of the Unit of the Scientific Research Projects of the Gaziosmanpaşa University.

References

[1] A. Cieszynska, M. Wisniewski, Extraction of palladium(II) from chloride solutions with CyphosIL 101/toluene mixtures as novel extractant, Sep. Purif. Technol. 73 (2010) 202–207.

[2] B.G. Zyłkiewicz, M. Kozłowska, Solid phase extraction using immobilized yeast *Saccharomyces cerevisiae* for determination of palladium in road dust, Anal. Chim. Acta 539 (2005) 61–67.

[3] T. Hees, B. Wenclawiak, S. Lusting, P. Schramel, M. Schwarzer, M. Schuster, D. Verstraete, R. Dams, E. Hemers, Distribution of platinum group elements (Pt, Pd, Rh) in environmental and clinical matrices: Composition, analytical techniques and scientific outlook, Environ. Sci. Pollut. Res. 5 (1998) 105–111.

[4] T. Shamspur, Solid phase extraction of trace amounts of palladium ions using multiwalled carbon nanotube modified by N, N´-bis(2-hydroxybenzylidene)-2,2´ (aminophenylthio) ethane prior to determination by flame atomic absorption spectrometry, Bull. Chem. Soc. Ethiop. 26 (2012) 19–26.

[5] N. Ozturk, V.N. Bulut, C. Duran, M. Soylak, Coprecipitation of palladium(II) with 1,5-diphenylcarbazite–copper(II) and determination by flame atomic absorption spectrometry, Desalination 270 (2011) 130–134.

[6] D. Afzali, R. Jamshidi, S. Ghaseminezhad, Z. Afzali, Preconcentration procedure trace amounts of palladium using modified multiwalled carbon nanotubes sorbent prior to flame atomic absorption spectrometry, Arab. J. Chem. 5 (2012) 461–466.

[7] P. Liang, E. Zhao, F. Li, Dispersive liquid–liquid microextraction preconcentration of palladium in water samples and determination by graphite furnace atomic absorption spectrometry, Talanta 77 (2009) 1854–1857.

[8] M. Mirzaei, M. Behzadi, N.M. Abadi, A. Beizaei, Simultaneous separation/preconcentration of ultra trace heavy metals in industrial wastewaters by dispersive liquid–liquid microextraction based on solidification of floating organic drop prior to determination by graphite furnace atomic absorption spectrometry, J. Hazard. Mat. 186 (2011) 1739–1743.

[9] Q. Hu, X. Yand, Z. Huang, J. Chen, G. Yang, Simultaneous determination of palladium, platinum, rhodium and gold by on-line solid phase extraction and high performance liquid chromatography with 5-(2-hydroxy-5-nitrophenylazo)thiorhodanine as pre-column derivatization regents, J. Chromatogr. A 1094 (2005) 77–82.

[10] Y. Yamini, M. Rezaee, A. Khanchi, M. Faraji, A. Sal, 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 (2010) 2358–2364.

[11] L. Tavakoli, Y. Yamini, H. Ebrahimzadeh, A. Nezhadali, S. Shariati, F. Nourmohammadian, Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES, J. Hazard. Mat. 152 (2008) 737–743.

[12] M. Muzikar, C. Fontàs, M. Hidalgo, J. Havel, V. Salvadó, A preconcentration system using polyamine Metalfix-Chelamine resin for the on-line determination of palladium(II) and platinum(IV) by inductively coupled plasma optical emission spectrometry, Talanta 70 (2006) 1081–1086.

[13] M.V.B. Krishna, M. Ranjit, K. Chandrasekaran, G. Venkateswarlu, D. Karunasagar, On-line preconcentration and recovery of palladium from waters using polyaniline (PANI) loaded in mini-column and determination by ICP-MS: Elimination of spectral interferences, Talanta 79 (2009) 1454–1463.

[14] M. Ghaedi, M. Montazerozohori, N. Rahimi, M.N. Biysreh, Chemically modified carbon nanotubes as efficient and selective sorbent for enrichment of trace amount of some metal ions, J. Ind. Eng. Chem. 19(5) (2013) 1477–1482.

[15] M. Ghaedi, K. Niknam, S. Zamani, H.A. Larki, M. Roosta, M. Soylak, Silica chemically bonded N-propyl kriptofix 21 and 22 with immobilized palladium nanoparticles for solid phase extraction and preconcentration of some metal ions, Mat. Sci. Eng. C 33(6) (2013) 3180–3189.

[16] M. Roosta, M. Ghaedi, A. Daneshfar, R. Sahraei, A. Asghari, Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology, Ultrason. Sonochem. 21 (2014) 242–252.

[17] M. Ghaedi, M. Montazerozohori, E. Nazari, R. Nejabat, Functionalization of multiwalled carbon nanotubes for the solid-phase extraction of silver, cadmium, palladium, zinc, manganese and copper by flame atomic absorption spectrometry, Hum. Exp. Toxicol. 32(7) (2013) 687–697.

[18] T. Revathi Reddy, N.N. Meeravali, A.V.R. Reddy, Novel reverse mixed micelle mediated transport of platinum and palladium through a bulk liquid membrane from real samples. Sep. Purif. Technol. 103 (2013) 71–77.

[19] J. Škrlíková, V. Andruch, I.S. Balogh, L. Kocúrová, L. Nagy, Y. Bazel̆, A novel, environmentally friendly dispersive liquid–liquid microextraction procedure for the determination of copper, Microchem. J. 99 (2011) 40–45.

[20] A.B. Tabrizi, Development of a dispersive liquid–liquid microextraction method for iron speciation and determination in different water samples, J. Hazard. Mat. 183 (2010) 688–693.

[21] Y. Assadi, M.A. Farajzadeh, A. Bidari, Dispersive liquid–liquid microextraction, Compr. Sample Sample Prep. 2 (2012) 181–212.

[22] S. Dadfarnia, A.M.H. Shabani, Recent development in liquid phase microextraction for determination of trace level concentration of metals, Anal. Chim. Acta 658 (2010) 107–119.

[23] A. Zgoła-Grześkowiak, T. Grześkowiak, Dispersive liquid–liquid microextraction, Trends Anal. Chem. 30 (2011) 1382–1399.

[24] P.X. Baliza, L.S.G. Teixeira, V.A. Lemos, A procedure for determination of cobalt in water samples after dispersive liquid–liquid microextraction. Microchem. J. 93 (2009) 220–224.

[25] H. Chen, P. Dua, J. Chen, S. Hu, S. Li, H. Liu, Separation and preconcentration system based on ultrasonic probe-assisted ionic liquid dispersive liquid–liquid microextraction for determination trace amount of chromium(VI) by electrothermal atomic absorption spectrometry, Talanta 81 (2010) 176–179.

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

[27] M. Gharehbaghi, F. Shemirani, Ionic liquid-based dispersive liquid–liquid microextraction and enhanced spectrophotometric determination of molybdenum (VI) in water and plant leaves samples by FO-LADS, Food Chem. Toxicol. 49 (2011) 423–428.

[28] M.H. Mallah, F. Shemirani, M.G. Maragheh, Ionic liquids for simultaneous preconcentration of some lanthanoids using dispersive liquid–liquid microextraction technique in uranium dioxide powder, Environ. Sci. Technol. 43 (2009) 1947–1951.

[29] J.J. Ma, X. Du, J.W. Zhang, J.C. Li, L.Z. Wang, Ultrasound-assisted emulsification–microextraction combined with flame atomic absorption spectrometry for determination of trace cadmium in water samples, Talanta 80 (2009) 980–984.

[30] D. Citak, M. Tuzen, Separation and determination of copper in bottled water samples by combination of dispersive liquid-liquid microextraction and microsample introduction flame atomic absorption spectrometry, J. AOAC Int. 96(6) (2013) 1435–1439.

[31] F. Shah, T.G. Kazi, Naeemullah, H.I. Afridi, M. Soylak, Temperature controlled ionic liquid-dispersive liquid phase microextraction for determination of trace lead level in blood samples prior to analysis by flame atomic absorption spectrometry with multivariate optimization, Microchem. J. 101 (2012) 5–10.

[32] X. Wen, L. Kong, M. Chen, Q. Deng, X. Zhao, J. Guo, A new coupling of spectrophotometric determination with ultrasound-assisted emulsification dispersive liquid–liquid microextraction of trace silver, Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 97 (2012) 782–787.

[33] S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, Spectrochim. Acta B 64 (2009) 666–671.

[34] M. Mohamadi, A. Mostafavi, A novel solidified floating organic drop microextraction based on ultrasound-dispersion for separation and preconcentration of palladium in aqueous samples, Talanta 81 (2010) 309–313.

[35] T.A. Kokya, K. Farhadi, Optimization of dispersive liquid–liquid microextraction for the selective determination of trace amounts of palladium by flame atomic absorption spectroscopy, J. Hazard. Mat. 169 (2009) 726–733.

[36] M. Soylak, M. Tuzen, Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations, J. Hazard. Mat. 152 (2008) 656–661.

[37] R.S. Praveen, S. Daniel, T.P. Rao, S. Sampath, K.S. Rao, Flow injection on-line solid phase extractive preconcentration of palladium(II) in dust and rock samples using exfoliated graphite packed microcolumns and determination by flame atomic absorption spectrometry, Talanta 70 (2006) 437–443.

[38] M. Vaezzadeh, F. Shemirani, B. Majidi, Microextraction technique based on ionic liquid for preconcentration and determination of palladium in food additive, sea water, tea and biological samples, Food Chem. Toxicol. 48 (2010) 1455–1460.