Use of Fe₃O₄ Nanoparticles and Ultrasound-assisted Dispersive Liquid-liquid Microextraction of Lead in Water, Tobacco, and Fertilizer Samples for FAAS Determination

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INTRODUCTION

Heavy metals contamination of water, soil, air, dust, and food leads to their bioaccumulation in animals and humans. In addition, the non-biodegradable nature of these metals makes them a major worldwide problem (1-5). Of these metals, lead is carcinogenic to human organs and harmful at even low concentrations (6,7). Exposure to lead causes learning disabilities in children due to its negative effects on brain development (8,9). The main sources of lead exposure to humans are water, air, dust, and food (10). Therefore, the accurate and precise determination of lead in environmental samples is important (11,12).

Sample pretreatment of these samples are necessary because of matrix interference and due to the low levels of lead present in these samples, which are below the detection limit of most available analytical instruments (13). There are many methods for separating and enriching pollutants in samples before their instrumental detection including solid-phase extraction (SPE) (14,15), liquid-liquid extraction (LLE) (16), coprecipitation (17), solid-phase microextraction (SPME) (18), liquid-phase microextraction (LPME) (19), and dispersive liquid-liquid microextraction (DLLME) (20-22). DLLME has

ABSTRACT

A Fe₃O₄ nanoparticle and ultrasonic coupled dispersive liquid-liquid microextraction (NPsU-DLLME) method was developed for the preconcentration of lead from water, tobacco, and fertilizer samples. Imidazole-2,4-dicarboxylic acid was used as the chelating agent and carbon tetrachloride as the extractor solvent. Addition of certain amounts of Fe₃O₄ nanoparticles and specific exposure periods to ultrasonic waves were optimized. Maximum recovery (%) was obtained using the following conditions: 17.5 mL sample volume, sample pH 6, 100 µL of carbon tetrachloride as the extraction solvent, 70 µL of ethanol as the dispersing solvent, 100 µL of 0.1% imidazole-2,4-dicarboxylic acid as the chelating agent, 100 µL of a 0.1% Fe₃O₄ nanoparticle suspension, and a 1-minute exposure to ultrasonic waves. This method was validated using an SPS-WW2 Wastewater certified reference material. The limit of detection (LOD) was 5.3 µg L⁻¹, the limit of quantification (LOQ) 15.8 µg L⁻¹, and the relative standard deviation (RSD) 2.6%. The method was applied to the determination of lead in some water, tobacco, and fertilizer samples.

received significant interest due to its short extraction time and low solvent usage (23,24). This method depends on forming a cloudy solution by dispersing an organic solvent. These conditions allow the analyte to move into the organic

phase after complexing with a chelating agent (25). However, reduction of the extraction time and solvent usage in DLLME is an on-going research area (26-28).

In this work, we propose a DLLME procedure combined with Fe₃O₄ nanoparticles and ultrasonic waves for the determination of trace amounts of Pb(II) as imidazole-2,4-dicarboxylic acid complex. This requires less dispersing solvent and less time prior to the micro-sampling flame atomic absorption spectrometric (FAAS) determination.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 3110 flame atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA), equipped with an air-acetylene flame and hollow cathode lamp, was used to measure the lead concentrations. The instrumental parameters were adjusted as recommended by the manufacturer. The samples were injected into the AAS with a Teflon® funnel using a homemade micro-sample introduction system. The signal was measured based on the peak height in the continuous aspiration mode (31,32). The instrumental operating conditions are listed in Table I.

A Nel pH-900 (Ankara, Turkey) and Metrohm pH meter (Model 691, Switzerland) with a combined glass electrode was used for the pH measurements. An ALC PK 120 Model centrifuge (Buckinghamshire, England) was used during

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centrifugation. A vortex mixer (VWR International LLC, USA) and an ultrasonic bath (Sonorex, Model No. DT-255, Bandelin Co., Germany) were used.

Chemicals and Reagents

All chemicals were of analytical grade. Distilled and deionized water with $18 \text{ M}\Omega\text{-cm}^{-1}$ resistivity were prepared using a Milli-Q® system (Millipore Corporation, USA). Standard Pb(II) solutions (1000 mg L^{-1}) were prepared by dissolving the nitrate salt in water (E. Merck, Darmstadt, Germany). Working standard solutions were obtained via the serial dilution of a stock standard solution. The 1.0% (w/V) imidazole-2,4-dicarboxylic acid (Sigma-Aldrich, St. Louis, MO, USA) solution was prepared using deionized water.

Fe_3O_4 nanoparticles were synthesized as previously reported (29, 30). Generally, 5.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 50 mL of deionized water. Afterwards, argon gas was passed through the solution for 15 minutes at 80°C . Then, 10 mL of concentrated NH_3 was slowly added to the solution using a dropping funnel. The Fe_3O_4 nanoparticles formed into a pure black solid product, which was removed after 15 minutes with a magnet, then washed three times with a 50-mL 0.1 mol L^{-1} NaCl solution and once with ethanol before drying at 80°C in an oven for 24 hours.

Microextraction Procedure

A 17.5-mL solution containing Pb(II) was placed into a 50-mL centrifuge tube before adding 2 mL of a phosphate buffer and adjusting the sample pH to 6.0 using dilute NaOH and HCl solutions. A 100- μL suspension of Fe_3O_4 nanoparticles (0.1%) in deionized water and 100 μL of 1.0% imidazole-2,4-dicarboxylic acid were added. 200 μL of the carbon tetrachloride extraction solvent was mixed with 70 μL of

ethanol and rapidly injected using a 5.0-mL syringe. The mixture was exposed to ultrasonic waves for 1 minute. During this step, a cloudy solution formed. The mixture was immediately centrifuged for 10 minutes at 4000 rpm. The upper aqueous phase was removed using a syringe; the extractant volume was diluted to 400 μL using concentrated HNO_3 . Then, 50 μL of the solution was introduced to the nebulizer of FAAS using a micro-injection system.

Applications

Water samples were collected from various regions in Turkey. The samples were filtered through 0.45- μm membrane filters. The procedure given above was then used for all samples. The same procedure was also applied to a SPS-WW2 Wastewater certified reference material obtained from Spectrapure Standards AS, Oslo, Norway.

Tobacco and fertilizer samples were purchased from local markets in Kayseri, Turkey. These samples were digested as described in (33) as follows: First, the samples were washed with deionized water and dried at 60°C . Then, 0.50 g from each sample was weighed into separate beakers. After adding 15 mL of concentrated nitric acid to the beakers, they were heated to dryness on a hot plate at 100°C . Then

the residues were cooled, digested with 10 mL concentrated HNO_3 and 5 mL of H_2O_2 , and heated again until dry. The mixture was dissolved in deionized water, filtered, and used as the real samples for application of the proposed method.

RESULTS AND DISCUSSION

Optimization of pH

The pH of the sample solution reportedly affects the complex formation between the analytes and the complexing agents; therefore, the sample pH significantly influences the DLLME procedure (34, 35). In this work, the lead solution pH was examined across the pH range from 2.0–8.0 during the microextraction procedure. The results are depicted in Figure 1. The pH of 6.0 was best suited for the quantitative recovery and was selected for further experiments.

Optimization of Chelating Agent Volume

In the proposed DLLME procedure, the volume of the (1.0%) imidazole-2,4-dicarboxylic acid was optimized. The results shown in Figure 2 indicate that 100 μL of the (1.0%) imidazole-2,4-dicarboxylic acid was enough to quantitatively recover Pb(II) and was chosen for further experiments. Reportedly, there should be sufficient chelation

Fig. 1. Effect of pH on the Pb(II) (%) recovery.

agent to catch all of the analytes because DLLME depends on the complexes between the analytes and the chelating agent (25).

Effect of Fe_3O_4 Nanoparticles on Reducing the Dispersing Solvent

In the present work, the Fe_3O_4 nanoparticle (0.1%) water suspension volume was optimized. The results are depicted in Figure 3. Approximately 100 μL of the nanoparticles provides a quantitative recovery for Pb(II). Excess Fe_3O_4 nanoparticles decrease the % recovery. Therefore, 100 μL of the suspended Fe_3O_4 nanoparticles was used for further work.

The influence of the added Fe_3O_4 nanoparticles on the volume of ethanol needed as a dispersing solvent was also studied. Figure 4 shows that quantitative recovery of Pb(III) occurred with low amounts of dispersing solvent (70 μL) with the addition of 100 μL Fe_3O_4 nanoparticles. In the absence of the Fe_3O_4 nanoparticles, 2000 μL of ethanol was required for the quantitative recovery of Pb(II).

Based on these results, DLLME can operate using low amounts of dispersing solvent. This finding is very promising for analytical and environmental chemistry because use of low solvent volume is one

way towards green chemistry and a safe environment.

Optimization of Ultrasonication Time

The application of ultrasonic waves during the microextraction procedure improves (%) recovery (26). Therefore, in the present work, ultrasonic exposure times from 0–5 minutes were studied. It was found that 1 minute is suitable for obtaining quantitative recovery, while an increase in ultrasonic exposure time decreases the (%) recovery. The reason may be that excess ultrasonic exposure destroys the lead imidazole-2,4-dicarboxylic acid complex and allows lead to retransfer into the aqueous phase. Therefore, a 1-minute ultrasonic exposure was chosen for further experiments.

Optimization of Extraction Solvent and Volume

An efficient extraction solvent in DLLME has to have low water solubility. This allows the formation of a cloudy solution of small droplets and leads to a high recovery (36, 37). The extraction solvents of carbon tetrachloride, chloroform, and dichloromethane were tested and yielded recoveries of 99%, 57%, and 67%, respectively. Thus, CCl_4 was selected for further works. In addition, amounts of 50, 100, 150, 200,

and 300 μL of carbon tetrachloride were examined. 100 μL of CCl_4 was sufficient for a quantitative recovery of Pb (100%) (Figure 5).

Optimization of Sample Volume

The sample solution volume significantly affects the DLLME performance due to its influence on the pre-concentration factor and the limit of detection. In the present work, sample volumes ranging from 10–50 mL were tested. A quantitative recovery was obtained using volumes of up to 17.5 mL. The pre-concentration factor was 43.75 when the sample and final volumes were 17.5 mL and 400 μL , respectively.

Influences of Coexisting Ions

Coexisting ions may interfere with the analyte and reduce the (%) recovery. Therefore, it is important to evaluate the effects of the most common coexisting ions on the performance of the extraction method (38–45). The influence of K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , CO_3^{2-} , NO_3^- , SO_4^{2-} , F^- , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Fe^{2+} , and Zn^{2+} were tested under optimum conditions. Table I shows that the Pb(II) recoveries were quantitative across the 94–100% range. These results also indicate that the proposed NPsU-DLLME method is matrix-independent.

Fig. 2. Effect of imidazole-2,4-dicarboxylic acid on the Pb(II) (%) recovery.

Fig. 3. Effect of Fe_3O_4 nanoparticles on the Pb(II) (%) recovery.

Fig. 4. Effect of Fe_3O_4 nanoparticles on the amount of ethanol required as a dispersing solvent.

Fig. 5. Effect of the carbon tetrachloride volume on the Pb(II) (%) recovery.

Analytical Figures of Merit

The proposed NPsU-DLLME procedure was evaluated to ensure its accuracy. The addition/recovery test results for the tap water samples are listed in Table II and clearly show that the proposed NPsU-DLLME procedure is highly efficient for recovering 97.8% lead. Furthermore, a SPS-WW2 Wastewater certified reference material was analyzed, and the results in Table III show a quantitative recovery of 103.5%.

The analytical performance of the presented procedure was checked using 15 mL of the model solution. The limit of detection (LOD), calculated as seven times the standard deviation of the blank, was $5.3 \mu\text{g L}^{-1}$. The limit of quantification (LOQ), calculated as three times the LOD, was $15.8 \mu\text{g L}^{-1}$. The relative standard deviation (%RSD), determined by using a Pb(II) solution ($30 \mu\text{g L}^{-1}$), was 2.6% ($N=7$).

Application to Real Samples

This work applied the proposed NPsU-DLLME procedure for determining lead in groundwater, dam water, wastewater, tobacco, and fertilizer samples. The results are

TABLE I
Effect of coexisting ions on Pb(II) (%) Recovery ($N=3$)

Ions	Concentration (mg/L)	Added as:	Recovery (%)
K^+	2000	KCl	99 ± 1
Ca^{2+}	800	CaCl_2	99 ± 1
Mg^{2+}	800	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	94 ± 1
Na^+	800	NaCl	96 ± 1
Cl^-	2000	KCl	96 ± 1
CO_3^{2-}	2000	Na_2CO_3	97 ± 1
NO_3^-	2000	KNO_3	99 ± 1
SO_4^{2-}	500	Na_2SO_4	100 ± 0
F^-	500	NaF	97 ± 1
Co^{2+}	10	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	99 ± 1
Ni^{2+}	5	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100 ± 0
Cu^{2+}	10	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	96 ± 0
Cd^{2+}	10	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	96 ± 1
Fe^{2+}	5	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	95 ± 1
Zn^{2+}	5	$\text{Zn}(\text{NO}_3)_2$	96 ± 1

TABLE II
Addition/Recovery Study of Pb(II) From Tap Water Sample

Added (μg)	Found (μg)	Recovery (%)
0	0	-
1.25	1.26 ± 0.0	101
2.5	2.45 ± 0.1	97.8

TABLE III
Evaluation of Procedure to SPS-WW2 Wastewater CRM

Certified Value ($\mu\text{g L}^{-1}$)	Observed Value ($\mu\text{g L}^{-1}$)	Recovery (%)
200	207 ± 11	103.5

TABLE IV
Application of Proposed
NPsU-DLLME Procedure for
Water, Tobacco, and Fertilizer
Samples (N=3)

Sample	Concentration
Groundwater	$0.13 \pm 0.04 \mu\text{g L}^{-1}$
Dam Water	$0.20 \pm 0.07 \mu\text{g L}^{-1}$
Wastewater	$0.64 \pm 0.04 \mu\text{g L}^{-1}$
Tobacco	$8.82 \pm 0.11 \mu\text{g g}^{-1}$
Fertilizer	$3.81 \pm 0.04 \mu\text{g g}^{-1}$

Mean $\pm$ standard deviation.

presented in Table IV and confirm the high reproducibility of the method. Table V compares the presented procedure to previously reported methods for determining lead.

CONCLUSION

A preconcentration method using a low amount of dispersing solvent was developed based on combining dispersive liquid-liquid microextraction with Fe_3O_4 nanoparticles (NPsU-DLLME) and ultrasound. Imidazole-2,4-dicarboxylic acid was used for the extraction and preconcentration of Pb(II) from water, tobacco, and fertilizer samples before its determination via Flame AAS. The findings in the present work are promising for both analytical and environmental chemistry because use of low solvent volumes is favorable for green chemistry and a safe method for the environment.

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TABLE V
Comparison of Proposed NPsU-DLLME Procedure to Other Methods
for Lead Determination

Preconcentration Method - Detection Method	LOD ($\mu\text{g L}^{-1}$)	Reference
Membrane filtration	3.6	(17)
Coprecipitation-FAAS	2.6	(40)
TC-IL-ME- AAS	5.8	(34)
IL-DLLME-AAS	1.5	(31)
NPsU-DLLME-AAS	5.3	This study

REFERENCES

1. J. Zhang, Turk. J. Chem. 37, 987 (2013).
2. O. Sendil, N. Mohammed, and G. Somer, Turk. J. Chem. 36, 335 (2012).
3. Z.A. Al Othman, Molecules 15, 7482 (2010).
4. M. Tuzen, A. Sari, D. Mendil, and M. Soylak, J. Hazard. Mater. 169, 263 (2009).
5. R. Gurkan, T. Cepken, and H.I. Ulusoy, Turk. J. Chem. 36, 159 (2012).
6. O. Turkoglu, S. Saracoglu, and M. Soylak, Trace Elem. Electroly. 20, 225 (2003).
7. E.M. Gama, A.S. Lima, and V.A. Lemos, J. Hazard. Mater. 136, 757 (2006).
8. M. Ibrahim, A.A. Shaltout, D.E. Atta, A.F. Jalbout, and M. Soylak, J. Iran Chem. Soc. 6, 364 (2009).
9. S. Radi, S. Tighadouini, Y. Toubi, and M. Bacquet, J. Hazard. Mater. 185, 494 (2011).
10. E. Bobrowska-Grzesik, and A. Jakobi-Kolon, J. Food Compos. Anal. 21, 326 (2008).
11. M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazeri, and M. Soylak, J. Hazard. Mater. 166, 1441 (2009).
12. M.T. Naseri, M.R.M. Hosseini, Y. Assadi, and A. Kiani, Talanta 75, 56 (2008).
13. A. Sarafraz-Yazdi, and A. Amiri, Trends Anal. Chem. 29, 1 (2010).
14. M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, and M. Soylak, J. Hazard. Mater. 154, 128 (2008).
15. M. Habila, E. Yilmaz, Z.A. AlOthman, and M. Soylak, J. Ind. Eng. Chem. 20, 3989 (2014).
16. A. Yasuhara, H. Shiraishi, M. Nishikawa, T. Yamamoto, T. Uehiro, O. Nakasugi, T. Okumura, K. Kenmotsu, H. Fukui, M. Nagase, Y. Ono, Y. Kawagoshi, K. Baba, and Y. Noma, J. Chromatogr. 774A, 321 (1997).
17. M. Soylak and N.D. Erdogan, J. Hazard. Mater. 137, 1035 (2006).
18. M.R. Khalili, Y. Yamini, S. Shariati, and J.A. Jonsson, Anal. Chim. Acta 585, 286 (2007).
19. A.A. Nuhu, C. Basheer, and B. Saad, J. Chromatogr. 879B, 1180 (2011).
20. P. Viñas, N. Campillo, I. López-García, and M. Hernández-Córdoba, Anal. Bioanal. Chem. 406, 2067 (2014).
21. C.B. Ojeda and F.S. Rojas, Chromatographia 74, 651 (2011).
22. H. Yan, and H. Wang, J. Chromatogr. 1295A, 1 (2013).
23. M.A. Farajzadeh, M. Bahram, F. Jafary, and M. Bamorowat, Chromatographia 73, 393 (2011).
24. Z.A. AlOthman, M. Habila, E. Yilmaz, and M. Soylak, J. AOAC Int. 96, 1425 (2013).
25. M. Salahinejad and F. Aflaki, J. Chem. Health Risks 3, 55 (2013).
26. X. Song, J. Li, C. Liao, and L. Chen, Chromatographia 74, 89 (2011).
27. R. Leila, Y. Yadollah, S. Abolfazl, S. Shahram, and F. Mohammad, Microchim. Acta 177 119 (2012).
28. A. Zhao, X. Wang, M. Ma, W. Wang, H. Sun, Z. Yan, Z. Xu, and H. Wang, Microchim. Acta 177, 229 (2012).

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29. X. Liu, Z. Ma, J. Xing, and H. Liu, J. Magn. Magn. Mater. 270, 1 (2004).
30. E. Yilmaz and M. Soylak, Talanta 116, 882 (2013).
31. M. Soylak and E. Yilmaz, Desalination 275, 297 (2011).
32. S.R. Yousefi and F. Shemirani, Anal. Chim. Acta 669, 25 (2010).
33. Z.A. AlOthman, M. A. Habila, E. Yilmaz, and M. Soylak, Microchim. Acta. 177, 397 (2012).
34. J.J. Ma, X. Du, J.W. Zhang, J.C. Li, and L.Z. Wang, Talanta 80, 980 (2009).
35. Z.A. AlOthman, E. Yilmaz, M. Habila, A. Shabaka, and M. Soylak, Microchim. Acta 180 669 (2013).
36. C. Zhang, Y. Wang, X. Cheng, X. Xia, and P. Liang, J. Chin. Chem. Soc. 58, 919 (2011).
37. G. Khayatian, and K. Sharifi, J. Incl. Phenom. Macrocycl. Chem 79, 185 (2014).
38. S. Saracoglu, M. Soylak, and L. Elci, Acta Chim. Slov. 50, 807 (2003).
39. M. Soylak and M. Tuzen, J Hazard. Mater. 152, 656 (2008).
40. I. López-García, Y. Vicente-Martínez, and M. Hernández-Córdoba, Talanta 110, 46 (2013).
41. S. Saracoglu, M. Soylak, and L. Elci, Can. J. Anal. Sci. Spectros. 46, 123 (2001).
42. V.A. Lemos, G.S. do Nascimento, and L.S. Nunes, Water Air Soil Pollut. 226, 2 (2015).
43. A. Duran, M. Soylak, and S.A. Tuncel, Journal of Hazardous Materials, 155, 114 (2008).
44. M.R. Pourjavid, M. Arabieh, S.R. Yousefi, M.R. Jamali, M. Rezaee, M.H. Hosseini, and A.A. Sehati, Mat. Sci. Eng. C-Biomim 47, 114 (2015).
45. M. Tuzen, and M. Soylak, J. Hazard. Mater. 162, 724 (2009).