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Ligandless Extraction and Determination of Trace Amounts of Lead in Pomegranate, Zucchini and Lettuce Samples after Dispersive Liquid-Liquid Microextraction with Ultrasonic Bath and Optimization of Extraction Condition with RSM Design

Fariba Tadayon, Elmira Hassanlou, Hasan Bagheri, Mostafa Jafarian

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***Abstract*—**Heavy metals are released into water, plants, soil, and food by natural and human activities. Lead has toxic roles in the human body and may cause serious problems even in low concentrations, since it may have several adverse effects on human. Therefore, determination of lead in different samples is an important procedure in the studies of environmental pollution. In this work, an ultrasonic assisted-ionic liquid based-liquid-liquid microextraction (UA-IL-DLLME) procedure for the determination of lead in zucchini, pomegranate, and lettuce has been established and developed by using flame atomic absorption spectrometer (FAAS). For UA-IL-DLLME procedure, 10 mL of the sample solution containing Pb^{2+} was adjusted to pH=5 in a glass test tube with a conical bottom; then, 120 µL of 1-Hexyl-3-methylimidazolium hexafluoro phosphate (CMIM)(PF_6) was rapidly injected into the sample solution with a microsyringe. After that, the resulting cloudy mixture was treated by ultrasonic for 5 min, then the separation of two phases was obtained by centrifugation for 5 min at 3000 rpm and IL-phase diluted with 1 cc ethanol, and the analytes were determined by FAAS. The effect of different experimental parameters in the extraction step including: ionic liquid volume, sonication time and pH was studied and optimized simultaneously by using Response Surface Methodology (RSM) employing a central composite design (CCD). The optimal conditions were determined to be an ionic liquid volume of 120 µL, sonication time of 5 min, and pH=5. The linear ranges of the calibration curve for the determination by FAAS of lead were 0.1-4 ppm with R^2=0.992. Under optimized conditions, the limit of detection (LOD) for lead was 0.062 µg.mL^{-1}, the enrichment factor (EF) was 93, and the relative standard deviation (RSD) for lead was calculated as 2.29%. The levels of lead for pomegranate, zucchini, and lettuce were calculated as 2.88 µg.g^{-1}, 1.54 µg.g^{-1}, 2.18 µg.g^{-1}, respectively. Therefore, this method has been successfully applied for the analysis of the content of lead in different food samples by FAAS.

Fariba Tadayon is with the Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran. Iran (phone: +989122597394; e-mail: F_Tadayon@iau-tnb.ac.ir).

Elmira Hassanlou and Mostafa Jafarian are with the Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran. Iran.

Hasan Bagheri is with the Chemical Injuries Research Center, Baqiyatallah University of Medical Sciences, Tehran, Iran.

***Keywords*—**Dispersive liquid-liquid microextraction, Central composite design, Food samples, Flame atomic absorption spectrometry.

I. Introduction

LEAD has a toxic role in the body and can lead to serious problems and replace the vital nutrients from human body [1], [2]. The main target for the lead toxicity is the nervous system, both in adults and children [3]. Lead exposure causes small increase in blood pressure, particularly in middle-aged and older people and can induce anemia. Several different procedures have been used for the determination of lead such as: single-drop microextraction (SDME), solid-phase extraction (SPE), graphic furnace atomic spectrometry (GF-AAS), and FAAS [4]. These microextraction methods are effective for the preconcentration of trace amount of lead in real samples [5], [6]. Recently, dispersive liquid-liquid microextraction (DLLME), which is a fast and simple method, has been extensively used and it does not utilize large amounts of organic solvents, while the other methods suffer from some disadvantages such as: high cost, use large amounts of toxic reagents [7]-[9]. Ionic liquid is a non-inflammability and non-volatile green solvent and a worthy replacement for toxic solvents [10]-[12]. In this investigation, UA-IL-DLLME coupled to FAAS is simple, easy, and inexpensive method.

II. Experimental

A. Reagent and Solution

In this work, all chemicals used were of analytical grade. Acetonitrile, Ethanol, all salts used, and [CMIM][PF_6] were obtained from Merk. Stock standard solution of 1000 mg.L^{-1} Pb^{+2} was prepared from an appropriate amount of lead nitrate salt (E.Merk) in de-ionised water containing 1% of HNO_3 and was diluted as required. [CMIM][PF_6] was prepared in acetonitrile.

B. Instrument

An atomic absorption spectrometer (Varian model AA-240), equipped with a lead hollow cathode lamp, was used for

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the determination of lead. A Centrifuge (Kokusan model H-11n, Japan) was used to accelerate the phase separation process. A pH meter (Gp-353) was used for measuring and adjusting the pH. A 100 µL microsyringe (Hamilton) was used for the injection of ionic liquid extracting phase to the solution. An ultrasonic bath (RK-100, Germany) was used in the experiments.

C. Ligandless UA-IL-DLLME Procedure

For UA-IL-DLLME method, buffer solution was added to 10 mL of sample solution containing Pb^{+2} in the test tube with a conical bottom. After adjusting the pH, 120 µL of [CMIM][PF_6] with a microsyring was rapidly added to the solution. After that, the mixture was placed in an ultrasonic bath for 3-15 min, and then, the mixture was centrifuged at 3000 rpm for 5 min in order to separate these two phases. IL-phase was diluted with 1 cc ethanol and was determined by FAAS.

D. Real Samples Preparation

Pomegranate sample was purchased from Saveh in Iran, while Zucchini and Lettuce samples were purchased from Shahriyar in Iran. Samples were washed with the deionized water. After that, samples dried in oven at 60 °C for 8h and then digested the next day. 0.5 g of samples was weighted and transferred to Teflon bombs and 10 mL of concentrated HNO_3 (65%), and 5 mL of H_2O_2 (30%) were added. The samples were heated on a plate for 2h at 100 °C. Then, clear solution was obtained cooling the samples. After that, the samples were diluted with the deionized water, and lead was measured in real samples prepared with FAAS.

E. Experimental Design

pH(A), ionic liquid(B), and sonication time(C) are the most effective factors on UA-IL-DLLME procedure. CCD was used to measure the optimized values of these factors. According to the design, each of the three factors (A-C) was studied at three levels, such as: low, medium, and high levels (Table I). In this model, all experiments were repeated three times and led to 20 experimental runs [13].

TABLE I
FACTORS AND LEVELS USED IN THE CCD

Factor	-1	0	+1
pH	4	5	6
Ionic liquid	50	85	120
Sonication time	3	5	7

III. RESULT AND DISCUSSION

A. Optimization of (UA-IL-DLLME) Procedure Using(CCD)

Quadratic polynomial equation of lead was obtained (1). In this equation, A, B, and C parameters were pH, ionic liquid volume, and sonication time, respectively. Variables AB, AC, and BC were the interaction between parameters. A^2, B^2, and C^2 were the quadratic coefficients of each parameter.

$$R= 0.12+ 0.020A +0.012B -5.600\times10^{-3}C +1.625\times10^{-3}AB -3.750\times10^{-4}AC +2.625\times10^{-3}BC -0.059A^2 -4.773\times10^{-3}B^2 +1.727\times10^{-3}C^2 \quad (1)$$

Analysis of variance (ANOVA) was used to evaluate the significance of each parameters and interaction terms. By adjusting R^2 and R^{-2}, the quality of the equation was shown which has been written as a model. In this model, the adjusted R2 and R-2 were 0.9945 and 0.9896, respectively. The ANOVA summary showed that the present model was significant, with a p-value less than 0.0001 and F-value of 202.73. In this case, A, B, C, and A2 are the significant model terms [14]. The lack of fit P-value of 0.1693 implies the lack of fit is not significant with respect to the pure error (Table II).

The three-dimensional graphs are used to evaluate the interaction effect of two parameters on response. Fig. 1 (a) shows the response surface obtained by plotting the effect of pH and ionic liquid volume. According to the storage time in ultrasonic bath for 5 min as a central point, the maximum amount of absorbent for extraction of lead by ionic-liquid volume 120 µL at pH=5 was reported. Fig. 1 (b) reveals the response surface obtained by plotting the effect of pH and sonication time. According to the ionic liquid volume of 85 µL as a central point, the maximum amount of absorbent for extraction of lead by sonication time for 5minutes at pH=5 was reported. Fig. 1 (c) illustrates the response surface obtained by plotting effect of ionic liquid volume and sonication time. According to the pH=5 as a central point, the maximum amount of absorbent for extraction of lead by ionic liquid volume 120 µL at sonication time for 5 minutes was reported.

B. Analytical Characteristics of UA-IL-DLLME Method

Under the optimized experimental conditions, the linear range of the calibration curve for the measurement of lead was 0.1-4 ppm with R^2=0.992 by using FAAS. LOD, EF, and RSD for lead were calculated, 0.062 µg.mL^{-1}, 93, and 2.29%, respectively.

C. Interference Study

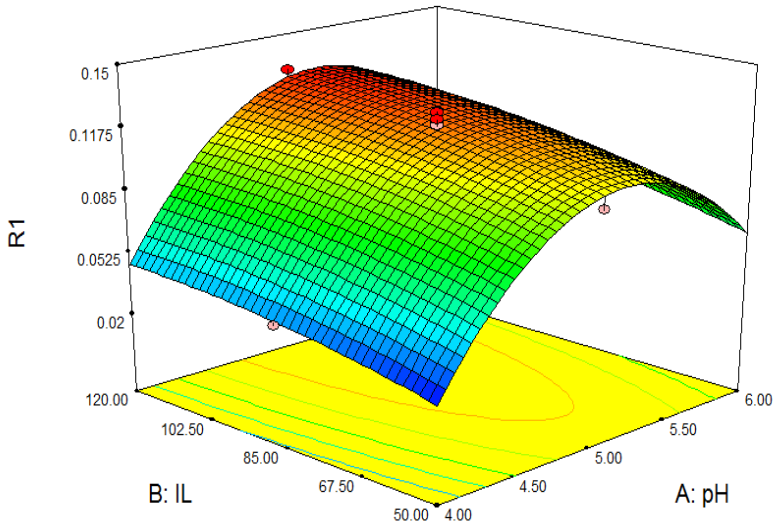
Under the optimized conditions, the effect of foreign ions in UA-IL-DLLME of Pb^{2+} was studied in the presence of several amounts of other ions. The effects of a number of ions such as: K^+, Mg^{+2}, Cu^{+2}, Na^+, Ni^{+2} on the preconcentration of lead ion were studied. In all studied ions, no interference was found from the concurrent ions for the measurement of lead.

D. Analysis of Real Samples

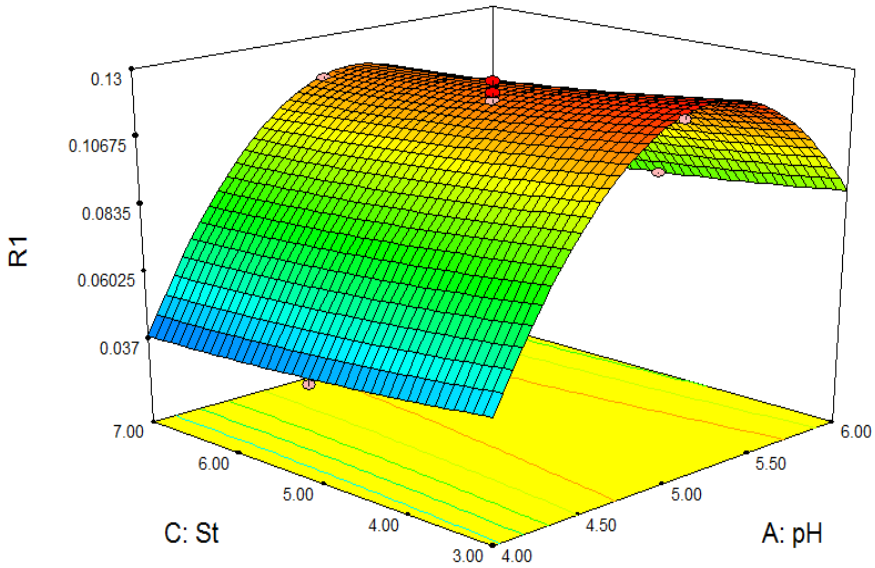
The UA-IL-DLLME method has been practical for the determination of lead in Pomegranate, Zucchini, and Lettuce samples. The results are given in Table IV.

TABLE II
ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Sum of Squares	df	Mean Square	F-Value	P-Value	Prob>F
Model	0.024	9	2.692E-003	202.73	<0.0001	significant
A- pH	4.040E-003	1	4.040E-003	304.29	<0.0001	
B-IL	1.369E-003	1	1.369E-003	103.10	<0.0001	
C-St	3.136E-004	1	3.136E-004	23.62	0.0007	
AB	2.113E-005	1	2.113E-005	1.59	0.2353	
AC	1.125E-006	1	1.125E-006	0.085	0.7769	
BC	5.513E-005	1	5.513E-005	4.15	0.0689	
A^2	9.499E-003	1	9.499E-003	715.46	<0.0001	
B^2	6.264E-005	1	6.264E-005	4.72	0.0550	
C^2	6.205E-006	1	8.205E-006	0.62	0.4500	
Residual	1.328E-004	10	1.328E-005			
Lack of fit	9.477E-005	5	1.895E-005	2.49	0.1693	Not significant
Pure Error	3.800E-005	5	7.600E-006			
Cor Total	0.024	19				

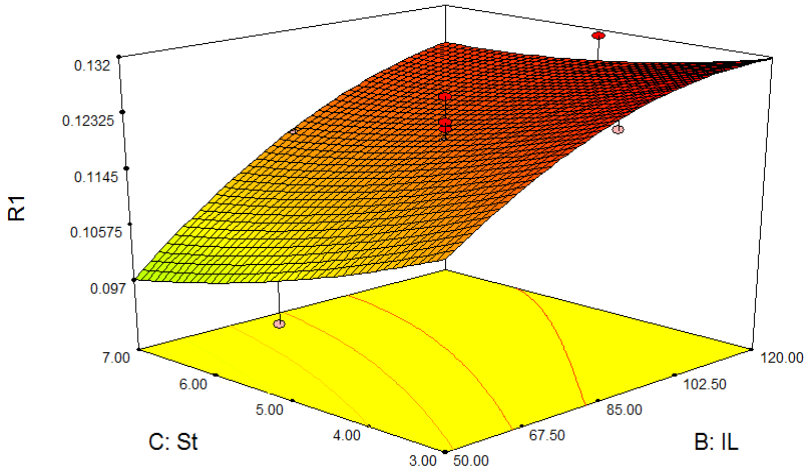


(a)



(b)

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(c)

Fig. 1 Response surfaces using CCD obtained by plotting:(a) pH vs ionic liquid volume, (b) pH vs sonication time, (c) ionic liquid volume vs sonication time

TABLE III
EFFECT OF FOREIGN IONS THE RECOVERY OF LEAD (0.01PPM, N=3)

Foreign Ion	Molar ratio (Ion/Pb^{+2})	Pb recovery (%)
K^{+}	100	100
Mg^{+2}	100	104
Cu^{+2}	1	100
Na^{+}	10	94.65
Ni^{+2}	1	98.41

TABLE IV
DETERMINATION OF LEAD IN POMEGRANATE, ZUCCHINI, LETTUCE (N=3)

Samples	FAAS(μg.g^{-1})	GT-AAS(μg.g^{-1})
Pomegranate	2.88	2.94
Zucchini	1.54	1.86
Lettuce	2.18	2.35

IV. CONCLUSION

In this study, the determination of Pb(II) in Pomegranate, Lettuce, and Zucchini samples by using UA-IL-DLLME method combined with FAAS was shown as an efficient and routine procedure. CCD method was used to optimize the affecting factors on UA-IL-DLLME. The important particularities of this method were low toxicity, low coast, simplicity, and rapidity. The proposed method has been successfully practical for the determination of lead in pomegranate, zucchini, and lettuce samples.

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