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Extraction Based on Dispersive Assisted by Ionic Liquids

Negin Fasih Ramandi and Farzaneh Shemirani

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1. Introduction

Determination of heavy metals in environmental, biological and in food samples has become of interesting subject because of their toxic effects on living beings [1, 2]. Despite good developments in the modern analytical instruments, direct determination of trace analytes at low concentrations is often a problem for analytical chemists and as a result, a sample preparation step is required. Therefore, preliminary preconcentration/separation step still remains as a bottleneck of the analytical procedure. Recent efforts on sample treatments techniques have involved following six general trends, namely: simplification, automation, miniaturization, expeditiousness, economical and safety aspects. The continuous quest for novel sample preparation procedures has led to the development of new methods, whose main advantages are their speed and negligible volume of solvents used as well as allowing sample extraction and preconcentration to be done in a single step. In this context, dispersive liquid liquid extraction (D-LLE) [3, 4] and dispersive solid phase extraction (D-SPE) [5] have been emerged as a response to those requirements that in some cases are unattainable with classical techniques. In spite of some strength points, these methods suffer from some drawbacks. For instance in D-LLE a problem still exists and that is continued reliance on using of toxic, hazardous, flammable and environmentally damaging organic solvents. Or typically in D-SPE, dispersion of sorbent in sample solution should assist by ultrasonic waves and phase separation needs to centrifuging step and as a result, extraction will be time consuming. Reducing the amount of organic solvents and using environmentally friendly solvents are the most important aims of analytical chemists. Due to the unique properties of ionic liquids (ILs), by using them in a proper way, these problems can overcome easily [6, 7].

Ionic liquids, emerging in recent years as novel stable and environmentally friendly compounds with amazing properties such as negligible vapor pressure, low flammability, and liquid state in a broad temperature range [8]. They are composed of asymmetrically substituted nitrogen-containing cations (e.g. imidazole, pyrrolidine, pyridine, etc.) with inorganic anions

(e.g. Cl^- , BF_4^- , PF_6^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, etc.). The range of available anion and cation combinations could provide too many different ILs, so at first glance; perhaps it is difficult to select the desired IL. But by considering some aspects, we can select the best IL based on desired application easily. These valuable materials have potential of using in term of D-LLE and D-SPE [6, 7]. D-LLE is a modified solvent extraction method which the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, a cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution is centrifuged and the fine droplets sediment at the bottom of the conical test tube [9]. Meanwhile, D-LLE based on ionic liquids is being recently considered as replacement for these solvents in sample preparation, due to their unique chemical and physical properties, good extractability for various organic compounds and metal ions as a neutral or charged complex, and miscibility with water and organic solvents. The performance of D-LLE based on ILs for preconcentration/separation of mercury in water samples has shown great improvement in sample treatment techniques which has been done earlier by our research team. This study provided simple, rapid, low cost and low toxicity extraction technique since only very small amounts of an IL as a green extraction solvent used as a replacement of environmentally damaging organic solvents [6].

D-SPE is based on the solid phase extraction (SPE) methodology, but the sorbent is directly added into the extract without conditioning. The clean-up is easily carried out by just shaking and centrifugation. The method was described as QuEChERS, which is the abbreviation of quick, easy, cheap, effective, rugged and safe. Recently our research team has improved D-SPE by using ionic liquid ferrofluids for monitoring lead in food and environmental samples [7].

Ferrofluids (FFs) are stable colloid dispersion of single-domain magnetic nanoparticles in a carrier liquid, which consist of three parts: ferromagnetic nanoparticles, coating of these nanoparticles and a carrier fluid [10]. The stability of the ferrofluid is due to the balance between repulsive (Brownian motions, steric and electrostatic forces) and attractive interactions (Van der Waals and dipolar attractive forces) [11]. The peculiarity of FF is the combination of normal liquid behavior with magnetic properties. As a result, wonderful applications in different fields such as biomedical [12], microelectronics [13], and also analytical chemistry [7, 14] have been reported.

Coating material prevents magnetic nanoparticles from agglomerating; on the other hand it has been proven that some chemical or physical surface modifications of coating material have improved its selectivity and/or affinity towards special target [14]. Therefore, not only the importance of coating material in FF is not deniable but also designs and production of ferrofluid with especial coating material is currently under intensive investigation [15]. For selecting an appropriate coating material, several criteria should be met. For instance, it should be non-toxic, low cost, chemically stable, and also compatible with carrier liquid. On the other hand to provide stable ferrofluid, a proper carrier solvent should have some properties. For instance, it should be immiscible with aqueous solution and have a low vapor pressure to prevent loss during extraction [16].

Due to the presence of electrostatic, hydrogen bonding and Van der Waals interactions, ILs possess unique structure, which provide a protective shell around magnetic nanoparticles and

improve ferrofluids stability greatly [17-19]. Therefore, by choosing ionic liquid as carrier fluid, very stable ferrofluid can be prepared (ionic liquid ferrofluid (IL-FF)), which is suitable for using in sample preparation methods. Due to rapid injection of an appropriate amount of IL-FF in to the aqueous sample by a syringe, extraction can be achieved within a few seconds. In addition, based on attraction of IL-FF to a magnet, there is no need to centrifuge for phase separation. Therefore, ionic liquid ferrofluid based dispersive solid phase extraction (IL-FF-D-SPE) provides very simple, rapid and low cost preconcentration/separation method [7, 14].

The importance of ionic liquids will be appeared more and more by discussing about their applications in dispersive liquid liquid extraction and also in dispersive solid phase extraction. Also in term of selectivity of ionic liquid ferrofluids some recent improvements which have been done by our research team, will be reported. The following key points in regards to application of ionic liquids in dispersive liquid liquid extraction and dispersive solid phase extraction are considerably noteworthy: simplicity, cost efficiency and suitability for batch operations (which could greatly shorten the sample preparation time).

2. Ionic liquid ferrofluid based dispersive solid phase extraction of lead from water, soil and rice samples

2.1. Lead; the occurrence, toxicity and methods of determination

Toxic effect of heavy metals on human life and the environment is one of the most important issues of our century and lead is one of the most hazardous members of the heavy metal family [20]. The increasing industrial use of lead in different fields such as: storage batteries, cable sheath and radiating shielding is contributing to the pollution of nature and using lead in gasoline antiknock products and paint pigments plays substantial role in contaminating the environment [21]. Due to its toxicity, non-biodegradability and tendency to accumulate in living organisms the regular absorption of trace amount of lead may have serious negative effects on humans (especially growing children) including: retardation of mental development, deficiencies in concentration and adverse effects on kidney function, blood chemistry and the cardiovascular system [22, 23]. Therefore, monitoring quantitative trace amount of lead in food, water and other environmental sample is inevitable.

Several analytical techniques have been reported in the literature for determination of lead such as: cloud-point extraction [1, 24], precipitation [25, 26], liquid-liquid extraction (LLE) [27], and solid-phase extraction (SPE) [28-30]. On one hand, SPE is widely used in the preconcentration methodology because of its simplicity, achievement of high recoveries, high sorption capacity, minimal costs due to low consumption of reagents and low extraction time [31]. On the other hand, in dispersive liquid-liquid extraction, as rather newly miniaturizing LLE, because an appropriate mixture of the extraction and disperser solvents are injected into the aqueous sample by a syringe, it is highly dispersed in the aqueous phase and extraction can be achieved within a few seconds [32]. Therefore, by using the advantages of these two techniques at the same time, ionic liquid ferrofluid-based dispersive solid phase extraction (IL-FF-D-SPE) as a new powerful extraction method was used for extraction of trace amount of lead in water, soil and rice samples [7].

2.2. Experimental

2.2.1. Instrumentation

A Varian model AA-400 atomic absorption spectrometer (Santa Clara, USA), equipped with an air-acetylene burner and with lead hollow cathode lamp was used for the determination of Pb(II). The lamp was operated at 5 mA, using the wavelength at 217.0 nm and slit of 1.0 nm, and the flow rates of air and acetylene were set as recommended by the manufacturer. Background correction has been used with a deuterium lamp. All measurements were carried out in peak height mode. A pH-meter Model 692 from Metrohm (Herisau, Switzerland) equipped with a glass combination electrode was used for the pH measurements. In addition, for magnetic separations, a strong neodymium-iron-boron (Nd₂Fe₁₂B) magnet (1.31 T) was used.

2.2.2. Reagents

All chemicals used were of analytical reagent grade unless otherwise stated. 1-Hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄ 98 %, 1-(2-pyridylazo)-2-naphthol (PAN), acetic acid, acetone, tetraethyl orthosilicate (TEOS), NH₃, ethanol, Pb(NO₃)₂ were purchased from Merck (Darmstadt, Germany). Standard stock solutions of Pb(II) were prepared by dissolving spectral pure grade chemical Pb(NO₃)₂ (1000 mg mL⁻¹ in 5 % HNO₃; Merck) in double distilled water with the addition of 5 mL of 12 mol L⁻¹ nitric acid and further diluted daily prior to use. Aqueous working solutions were prepared immediately before use by diluting with water. A solution of 4 × 10⁻⁷ and 8 × 10⁻⁶ and 4.2 × 10⁻⁶ mol L⁻¹ PAN were prepared by dissolving appropriate amount of this reagent in pure ethanol. Nano-Fe₃O₄ was purchased from Sigma-Aldrich (St. Louis, MO, USA) (Fe₃O₄ spheres powder, <40 nm, purity >98 %). Buffer solution (pH = 5.8, 1 mol L⁻¹) was prepared by mixing appropriate amount of potassium hydrogen phthalate and sodium hydroxide. High purity HNO₃ (65 %, ultra-pure, Merck), HClO₄ and HCl were used for the digestion of dust sample throughout this work.

2.2.3. Preparation of Ionic liquid ferrofluid and extraction procedure

In this work Fe₃O₄/SiO₂ NPs were used as a sorbent. It was synthesized as below. Briefly, 2.0 g of Fe₃O₄ nanoparticles were suspended in 200 mL ethanol under sonication for 1 h. Then, 40 mL of concentrated ammonia, 35 mL deionized water and 1 mL TEOS were added to the suspension. Next, for about 1 h the mixture was sonicated and finally approximately for 8 h was mixed vortex. The silica-coated nanoparticles (SCMNPs) were collected simply by magnetic separation and were thoroughly washed with deionized water three times and then dried, yielding nanoparticles a fine powder.

After preparing coated magnetic nanoparticle, one step was needed to prepare ionic liquid ferrofluid. In this context, 10 mg of silica-coated magnetic nanoparticles and 100 mL of acetic acid were mixed in a vial and were heated at 90 °C under stirring for approximately 45 min to allow acetic acid adsorption. Next, acetic acid-coated magnetic nanoparticles were dispersed in 0.1 gr 1-Hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄. To obtain ionic liquid

ferrofluid, the result suspension was sonicated for 30 min. The resulting suspension had a magnetite fraction of 9.1 %. Finally, IL-FF-D-SPE was done simply as below. The sample, or standard solution containing $40 \mu\text{g L}^{-1}$ of Pb(II), PAN ($4 \times 10^{-7} \text{mol L}^{-1}$), NaNO_3 (3.78 w/v%), and 1 mL buffer (pH = 5.8) were poured into a 50 mL tube. Then by using a 1.0 mL syringe, the ionic liquid ferrofluid was injected into the sample solution and a dark cloudy suspension was formed rapidly and the extraction process was quickly completed after approximately 6 seconds. Subsequently, a strong magnet was placed at the bottom of the tube to let the ionic liquid ferrofluid settle. After about 2 min, the solution became clear and limpid and supernatant was simply discarded by decanting. After removing the magnet, 1 mL nitric acid (2mol L^{-1}) was added to the vial to desorb the lead through the sonication. By using the magnet at the bottom of the vial, the clear solution containing of eluted metal ions was obtained. By transferring this limpid solution to the glass tube, the analyte in the eluent was determined by flame atomic absorption spectrometry (FAAS). A schematic view of IL-FF-D-SPE experimental set up is shown in Figure 1.

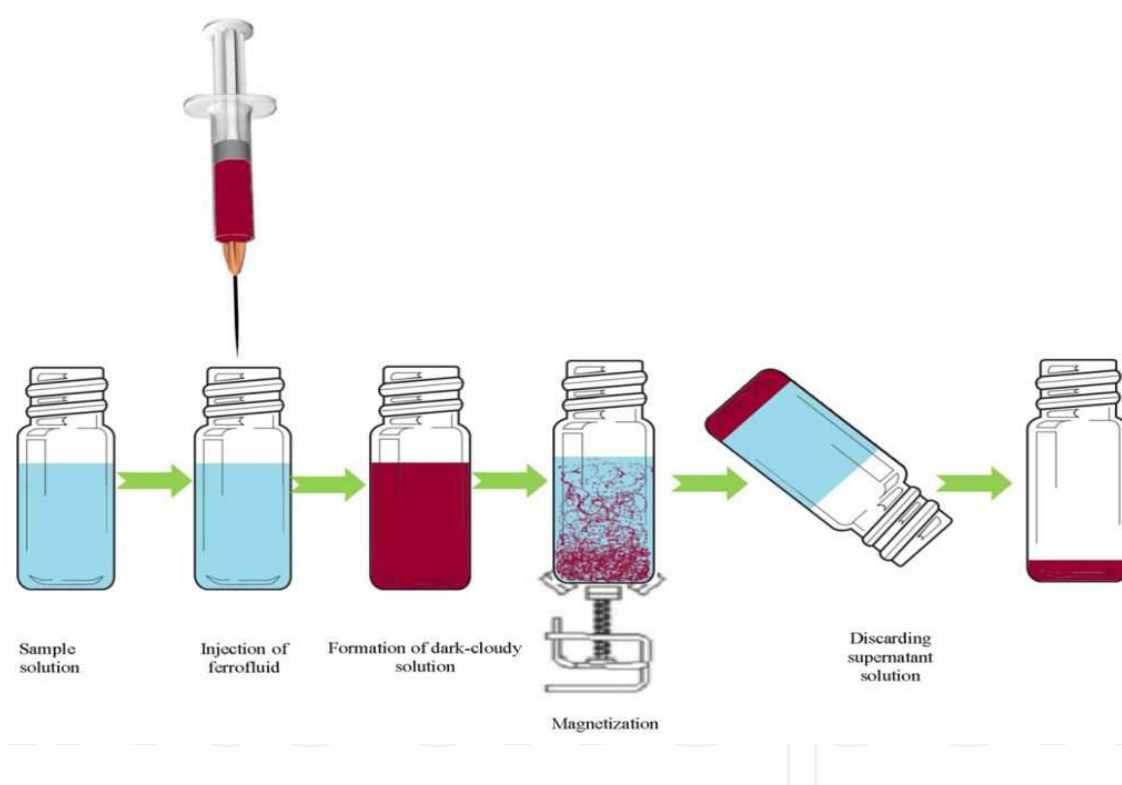


Figure 1. A schematic view of IL-FF-D-SPE experimental set up [7].

2.3. Result and discussion

2.3.1. Selection of ionic liquid for preparation of the ferrofluid: type and volume

When selecting an appropriate carrier (solvent), several criteria should be met. For instance, the solvent should be immiscible with aqueous solution and have a low vapor pressure to prevent loss during extraction. According to these criteria, some ionic liquids such as 1-

Hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄, 1-Hexyl-3-methylimidazolium hexafluorophosphate [Hmim]PF₆, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Hmim]Tf₂N, were selected and by the qualitative observation of sedimentation of each ferrofluid, the stability of the suspensions was checked.

For this purpose, in three vials, the same amount of coated magnetic nanoparticles added to the same amount of these three ionic liquids separately. After 30 min sonication, the stability of these three ferrofluids against sedimentation was investigated. As the result, only in the case of using [Hmim]BF₄ as the carrier, the ferrofluid maintained stable even after about 8 h. Therefore, [Hmim]BF₄ was selected as an environmentally friendly carrier to achieve stable ferrofluid.

When choosing the minimum volume of [Hmim]BF₄ for a quantitative extraction of Pb(II), the range of 0.1-0.3 g was determined. Finally, 0.1 g [Hmim]BF₄ was enough to preconcentration the metal ions, at the studied concentrations and using 50 mL of sample. For higher amount of [Hmim]BF₄, the extraction efficiency was almost constant.

2.3.2. Selection of eluent

Various types of solvents such as: acetone, ethanol, ethanol (1% HNO₃) and HNO₃ were examined in order to find the best eluent. Based on the desorption of Pb(II) from modified nanoparticles in the acidic medium, nitric acid was chosen as the best eluent.

2.3.3. Screening and optimization strategy

The effect of the following six factors namely pH, concentration of 1-(2-pyridylazo)-2-naphthol (PAN) as ligand to form complex with lead, sorbent amount, eluent volume, extraction time, ionic strength which effected the extraction recovery of Pb(II) was investigated with the help of chemometrics method. Therefore, in screening step by a half-factorial design these six factors were evaluated in two levels. The low and high values were selected from the results of previous experiments (Table 1).

Parameters	unit	Level	
		Low	High
pH (A)	-	4	8
Concentration of PAN (B)	(mol L ⁻¹)	4 × 10 ⁻⁷	8 × 10 ⁻⁶
Sorbent amount (C)	(gr)	0.01	0.06
Eluent volume (D)	(mL)	0.5	1
Extraction time (E)	(s)	2	6
Ionic strength (F)	(w/v %)	0	10

Table 1. The experimental factors and levels of them in ferrofluid- based D-SPE of Pb(II) [7].

By referencing the results of the ANOVA and Pareto charts, the main effects were selected. Evaluation of the normalized results of the experimental design was based on $P=95\%$ and the standard effect is estimated for computing a t-statistic for each effect. When its value is higher than $\pm t$, a parameter is considered as significant; otherwise the parameter is not significant in the studied range. The analysis of the results is visualized using standardized main effect Pareto charts ($P=95\%$) was shown in Figure 2. As it can be concluded from Figure 2, ionic strength and pH are effective parameters which have negative and positive effects on the extraction recovery respectively.

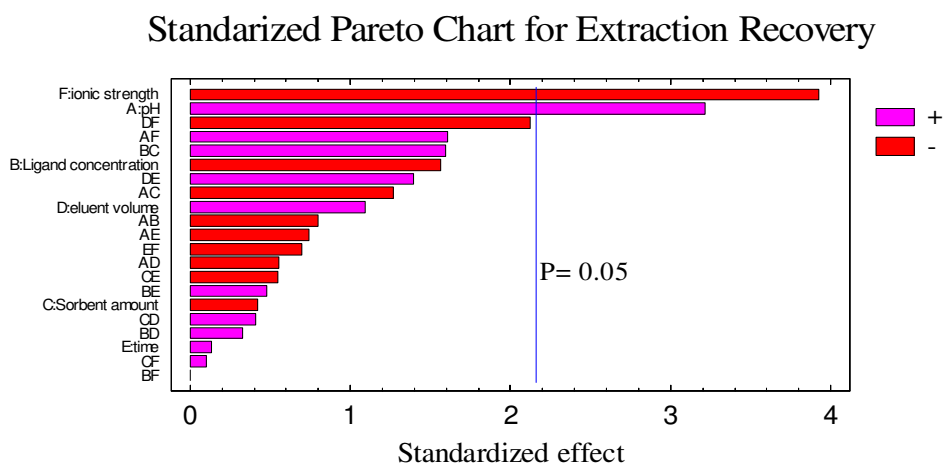


Figure 2. Standardized ($P=0.05$) Pareto chart, representing the estimated effects of parameters obtained from the half-fraction factorial design [7].

The results illustrated in Figure 2 also confirm that pH has significant effect on extraction recovery because it not only influences the surface active centers and charge of sorbent, but also affects the degree of ionization and solubilization of sorbate in aqueous solutions. According to Figure 2, extraction time has no significant effect on extraction recovery. This can be explained by the fact that based on the rapid injection of ferrofluid into the aqueous solution; the extraction was completed in only a few seconds. Due to the relatively large surface area, the highly active surface sites lead to a very fast mass transfer process and generally offer a fast extraction process. Therefore, time has no significant effect on extraction recovery. Based on these results, to continue the optimization; four insignificant parameters were fixed at appropriate amount (concentration of PAN: 4×10^{-7} mol L⁻¹, sorbent amount: 0.01 gr, eluent amount: 1 mL, time: 6 s).

The central composite design (CCD) was performed to evaluate the optimum condition of performance of ionic liquid Ferrofluid-based dispersive solid phase extraction of Pb(II) for the two significant parameters: pH and ionic strength. The number of experimental points (N) is defined by the expression: $N = 2^f + 2f + C_p$, where f is the number of variables and C_p is the number of center points. In this study, f and C_p were set at 2 and 3, respectively, which meant 11 experiments had to be done.

The 3D response surface plot and its related counter for the extraction recovery (%) were shown in Figure 3. As seen in Figure 3, the extraction recovery had an upward trend by increasing the pH and ionic strength and reached a peak value at pH 5.8 and ionic strength 3.78 (w/v %). Following that, the extraction recovery had a decline by increasing the pH and ionic strength. It is not surprisingly that pH 5.8 was chosen as the optimum pH value, because at lower pH values, ligand was protonated and at higher pH, Pb(II) could easily be precipitated with OH⁻, as a result in both cases the extraction recovery plummeted to minimum value.

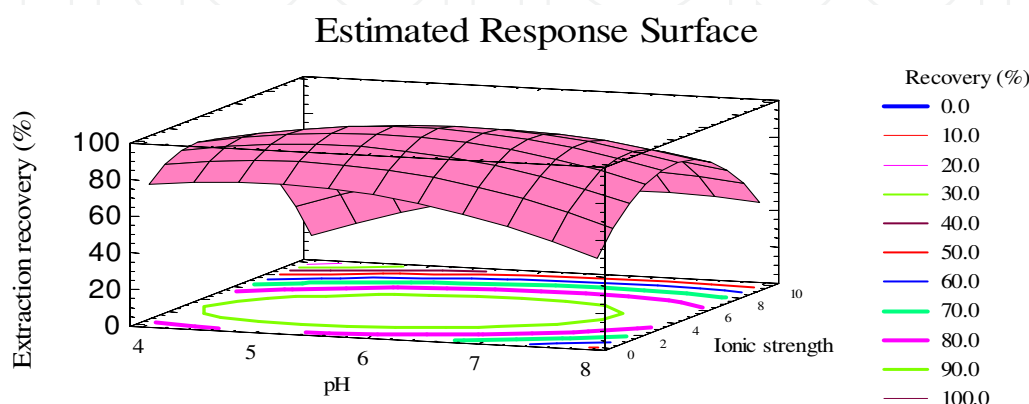


Figure 3. Estimated response surface by plotting extraction recovery (%) versus ionic strength and pH, with related contours [7].

2.3.4. Effect of potentially interfering ions

In order to assess the applications of the recommended procedure, the influences of possible matrix ions in the environmental samples and some transition metals on the recoveries of Pb(II) were also examined. By spiking appropriate amounts of potentially interfering ions in range of 50-10000 $\mu\text{g mL}^{-1}$ to 50.0 mL of solution containing 40 $\mu\text{g L}^{-1}$ of Pb(II) and excess amount of PAN at optimum condition, the effect of them in the natural water samples on the extraction recovery percent of Pb(II) were studied. A given species was considered to interfere if it resulted in a $\pm 5\%$ variation of the absorbance. Based on obtained results, no interference was observed for Na⁺, K⁺ and NO₃⁻ up to 10000 $\mu\text{g mL}^{-1}$, for Ni²⁺, Ag²⁺, Zn²⁺ and Ca²⁺ up to 1000 $\mu\text{g mL}^{-1}$, for Mg²⁺, Cu²⁺, Hg²⁺ and CO₃⁻ up to 100 $\mu\text{g mL}^{-1}$ and for some species such as: Pd²⁺, Fe²⁺ and Fe³⁺ up to 50 $\mu\text{g mL}^{-1}$. This results show that this preconcentration/separation method could be applied to the highly saline samples and the samples that contains some transition metals at $\mu\text{g mL}^{-1}$ levels.

2.3.5. Figures of merit and comparison of IL-FF-D-SPE with other methods

At the optimum condition the limit of detection (LOD) of 1.66 $\mu\text{g L}^{-1}$, linear range of 5-372 ng mL⁻¹, and also relative standard deviation of 1.34 % were achieved. The obtained results were compared with other literatures in Table 2. As it can be concluded from Table 2, in addition to

simplicity of this method (in comparison to a solid phase extraction), the presented IL-FF-D-SPE method has good limit of detection ($1.66 \mu\text{g L}^{-1}$), good repeatability (RSD %). The proposed method is much faster due to dispersion of sorbent in the aqueous phase also there is no need to shake the sample solution. Moreover, for phase separation, there was no need to centrifuge or conical the bottom glass tube, which can be easily damaged and are difficult to clean.

Sorbent	PF/EF ^a	LOD ^b ($\mu\text{g L}^{-1}$)	RSD ^c (%)	Linear range (ng mL^{-1})	Sorption capacity (mg g^{-1}) ^f	Extraction time (min)	Ref
Chromosorb101 (FAAS)	31	2.85	2.7	0.5- 10 ^d	7.50	10	[33]
MnO ₂ /CNTs (ETAAS)	100	4.4	3.2	-	6.7	2	[34]
Solid sulfur (FAAS)	250	3.2	4.7	10-300	15.6 ^e	33	[35]
Graphene (FAAS)	125	0.61	3.25	10-600	16.6	50	[36]
Amborsorb-572 (FAAS)	75	3.65	2	-	0.17 ^f	4.5 ^h	[37]
SCMNPs (FAAS)	200	1.66	1.34	5-372	10.66	6 ^s	This study

^a Preconcentration factor or enrichment factor.

^b Limit of detection.

^c Relative standard deviation.

^d mg L^{-1} .

^e $\mu\text{g g}^{-1}$.

^f mmol gr^{-1} .

^h Hour.

^s Second.

Table 2. Comparison of the published preconcentration methods for Pb(II) with the proposed method [7].

2.3.6. Analysis of real samples

After digestion of dust and rice sample according to previous report [38, 39] the standard addition method was applied for determination of trace amounts of Pb(II) in water, soil, and rice samples. Generally, the recoveries of Pd(II) ions were obtained in the range between 99.6-110.2 % (Table 3).

Sample	Spiked (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Mineral water ^a	0	ND ^e	-
	10	9.6 ± 0.2	96.0
	20	20.9 ± 0.5	104.5
Tap water ^b	0	ND	-
	10	10.3 ± 0.3	103.0
	20	21.3 ± 0.6	106.5
Road dust ^c	0	8.6 ± 0.4	-
	50	59.1 ± 0.9	118.2
Rice ^d	0	ND	-
	20	20.7 ± 0.5	103.5

^a Zam zam mineral water, Iran.

^b From drinking water system of Tehran, Iran.

^c From Niyayesh highway, Tehran, Iran.

^d From Mazandaran, Iran.

^e Not detected.

Table 3. Analytical result for determination of Pb(II) in different samples [7].

3. Selective ionic liquid ferrofluid based dispersive-solid phase extraction for simultaneous preconcentration/separation of lead and cadmium in milk and biological samples

3.1. Lead and Cadmium; the occurrence, toxicity and methods of determination

Determination of heavy metals in biological and in food samples has become a key interest because of their toxic effects on living beings [1]. Heavy metals such as Cd(II) and Pb(II) cause irreparable effects on the urinary tract, liver, blood chemistry and the cardiovascular system [40]. Several studies have been reported for separation/ preconcentration of Cd(II) and Pb(II) such as solid phase extraction [41, 42] liquid liquid extraction [43] and dispersive liquid liquid extraction [3, 4]. In spite of some benefits, these methods suffer from many drawbacks. Therefore, improvements are necessary. So for the first time our research team wanted to report a very simple, fast, efficient, and selective separation/ preconcentration method which is assisted by ionic liquid ferrofluid for cadmium and lead [14]. For this purpose, TiO₂ as an excellent coating material for magnetic nanoparticles was chosen and also improve its selectivity by loading 1-(2-pyridylazo)-2-naphtol on its surface. Additionally, to provide a stable ferrofluid, 1-Hexyl-3-methylimidazolium tetrafluoroborate was chosen as the carrier liquid. Therefore, selective ionic liquid ferrofluid based dispersive solid phase extraction (IL-FF-D-SPE) was used for separation/ preconcentration of cadmium and lead in milk, human urine, and blood plasma samples combined with FAAS which is a very fast, easy, cheap, and

selective determination technique in comparison with other methods such as ICP-MS. Additionally, different parameters which effected the extraction recovery of Pb(II) and Cd(II) were investigated with the help of chemometrics method [14]

3.2. Experimental

3.2.1. Instrumentation

The determination of Pb(II) and Cd(II) was carried out using a Varian Spectra AA-400 atomic absorption spectrometer (Santa Clara, USA), equipped with a deuterium background correction and an air-acetylene burner. The lamp currents were set at 5 and 4 mA for Pb(II) and Cd(II), respectively. All measurements were carried out in the peak height mode at 217.0 and 228.8 nm, using a spectral band width of 1.0 nm and 0.5 nm for Pb(II) and Cd(II), respectively. A pH-meter Model 692 from Metrohm (Herisau, Switzerland) equipped with a glass combination electrode was used for the pH measurements. Additionally, for magnetic separations, a strong neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{12}\text{B}$) magnet (1.31 T) was used. For separation of human blood plasma from a blood sample, a refrigerated centrifuge (Hettich, Universal 320R, Buckinghamshire, England) equipped with an angle rotor (6 place, 9000 rpm, cat no 1620A) was used.

3.2.2. Reagent

All chemicals used were of analytical reagent grade unless otherwise stated. The stock standard solutions of Cd(II) and Pb(II) (1000 mgL^{-1}) were prepared from appropriate amounts of their nitrate salts (Merck, Darmstadt, Germany) in ultra-pure water and working standard solutions were prepared by appropriate stepwise dilution of the stock standard solutions. 1-Hexyl-3-methylimidazolium tetrafluoroborate $[\text{Hmim}]\text{BF}_4$ 98 %, 1-Hexyl-3-methylimidazolium hexafluorophosphate $[\text{Hmim}]\text{PF}_6$, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[\text{Hmim}]\text{Tf}_2\text{N}$, 1-(2-pyridylazo)-2-naphthol, tetra-n-butyl orthotitanate (TBOT), NH_3 , ethanol, sodium dodecyl sulfate were purchased from Merck (Darmstadt, Germany). Nano- Fe_3O_4 was purchased from Sigma-Aldrich (St. Louis, MO, USA, Fe_3O_4 spheres powder, <40 nm, purity >98 %). Buffer solution ($\text{pH} = 6.7$, 1 molL^{-1}) was prepared by dissolving appropriate amounts of potassium dihydrogen phosphate (1 molL^{-1}) and sodium hydroxide (1 molL^{-1}). High purity HNO_3 , H_2O_2 , HClO_4 and HCl were purchased from Merck (Darmstadt, Germany), which were used for the digestion of milk, urine, and blood plasma samples throughout this project. The pipettes and vessels were cleaned before use by soaking in 10 % nitric acid solution for at least 24 hours and then rinsed thoroughly with distilled water.

3.2.3. Preparation of Ionic liquid ferrofluid and extraction procedure

To prepare TiO_2 coated Fe_3O_4 nanoparticles, first 10 mL of tetra-n-butyl orthotitanate was dissolved in 70 mL ethanol to form a clear solution. Then, 0.2 g Fe_3O_4 nanoparticles were dispersed in this solution under sonication for approximately 5 min. While the suspension stirred vigorously over a period of 15 min, a 1:5 (v/v) mixture of water and ethanol was added slowly with a dropper into this mixture. Then, the mixture was stirred further for 1 hour. Finally, after separating and washing the residue with ethanol, the obtained powder was oven-dried and calcinated at 200°C for 6 h. In the next step to immobilize 1-(2-pyridylazo)-2-naphthol

on sodium dodecyl sulfate-coated $\text{Fe}_3\text{O}_4/\text{TiO}_2$ the following procedure was done. In a 250 mL beaker, 1.0 g of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ nanoparticles were dispersed in 20 mL of 0.001 molL^{-1} HCl, under sonication. During sonication of this mixture, to avoid any changes in ionic strength, 0.3 mL of 1 molL^{-1} NaNO_3 was added using a dropper. The pH of the solution was adjusted to 5. Then, 3 mL of 1 molL^{-1} sodium dodecyl sulfate was added and solution was stirred for 1 h. After that 0.2 g 1-(2-pyridylazo)-2-naphtol was added and the solution was stirred for further 1 h at 60°C in a water-bath. Finally, the suspension result was filtered and dried under a vacuum.

To form a selective ionic liquid ferrofluid, 30 mg of modified titana-coated magnetic nanoparticles with 1-(2-pyridylazo)-2-naphtol and 100 mL acetic acid, as a stabilizing agent, were mixed in a vial. The mixture was stirred and heated at 90°C for approximately 45 min. Next, the resulted powder was dispersed in 0.3 g $[\text{Hmim}]\text{BF}_4$. After 30 min of sonication of this mixture, stable suspension of magnetic nanoparticles (ionic liquid-ferrofluid) was obtained.

Finally, the selective IL-FF-D-SPE was done simply as below. The sample, or standard solution contains $40 \mu\text{g L}^{-1}$ Pb(II) and $30 \mu\text{g L}^{-1}$ Cd(II), NaNO_3 (0% w/v), at pH 6.7 which were poured into a 50 mL tube. Then, by using a 1.0 mL syringe, the ionic liquid-ferrofluid, containing 0.03 g sorbent and 0.3 g ionic liquid was injected into the sample solution to form a dark cloudy suspension. Due to the rapid injection of the ferrofluid into the aqueous sample, extraction was achieved within a few seconds. By using a strong magnet at the bottom of tube, the ferrofluid was settled and the solution became clear. After removing the supernatant by decanting, 1 mL nitric acid (1.59 molL^{-1}) was added to the vial to desorb the Pb(II) and Cd(II) through 8 min sonication. Subsequently, a strong magnet was placed at the bottom of tube and immediately the solution became limpid. By using a syringe this clear solution was transferred to a vial for analyzing with FAAS.

A schematic view of selective ionic liquid ferrofluid based dispersive solid phase extraction is shown in Figure 4.

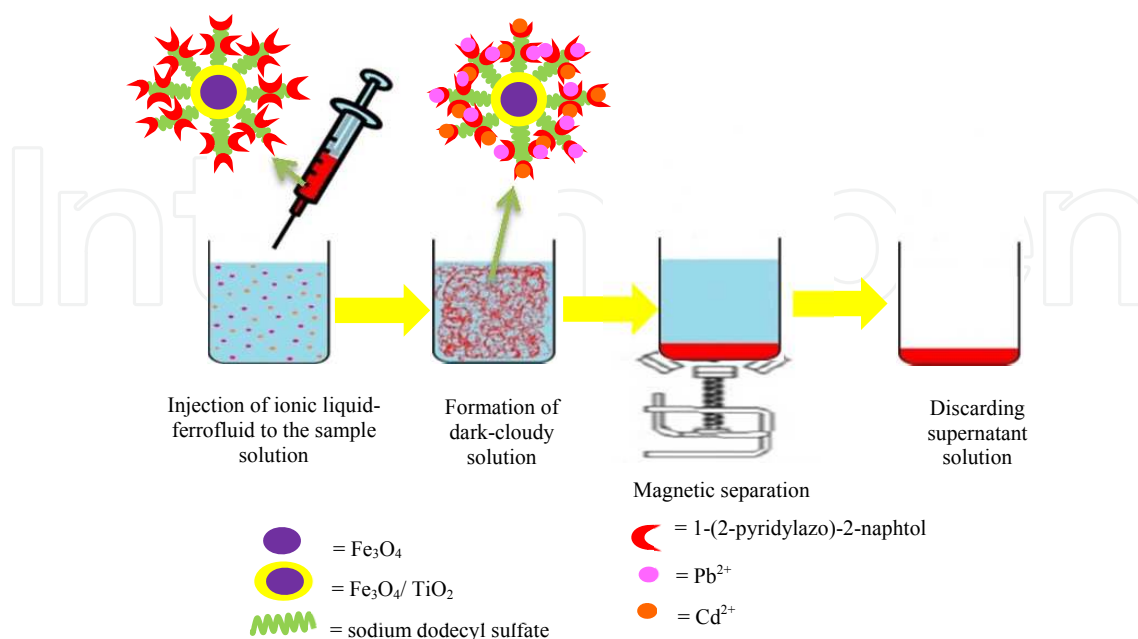


Figure 4. A schematic view of selective IL-FF-D-SPE experimental set up [14].

3.3. Result and discussion

3.3.1. Selection of ionic liquid for preparation of the ferrofluid

For selecting the best carrier fluid, apart from providing a stable ferrofluid, several criteria such as: immiscibility with an aqueous solution, non-toxicity, having low vapor pressure to avoid any loss during extraction, and compatibility with coating material should be met. For this purpose, some ionic liquids such as 1-Hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄, 1-Hexyl-3-methylimidazolium hexafluorophosphate [Hmim]PF₆, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Hmim]Tf₂N, were selected and by the qualitative observation of sedimentation of each ferrofluid, the stability of the suspensions was checked. Finally 1-Hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄ was chosen.

3.3.2. Selection of eluent

Based on the desorption of Pb(II) and Cd(II) from modified nanoparticles in the acidic medium, this medium would be preferred in desorption step. To avoid any losses of sorbent, chloric acid was not chosen because this acid can dissolve Fe₃O₄ nanoparticles. Also based on the possibility of formation of precipitate of lead in presence of sulfate ions, sulfuric acid was not chosen too. Therefore, the possibility of desorption of lead and cadmium ions in acidic medium was examined by using nitric acid. Also some organic solvent such as ethanol, ethanol (1% HNO₃) and acetone were selected to examine the possibility of desorption of these ions in organic medium. Based on the obtained result, nitric acid was chosen as the best eluent.

3.3.3. Screening and optimization strategy

In this study, Plackett-Burman screening design was used to select the variables that mainly effect the extraction recovery of Pb(II) and Cd(II). Based on the preliminary experiments, the effects of seven factors, at two levels were investigated. pH (4 and 8), sorbent amount (0.01 and 0.03 g), ionic liquid amount (0.3 and 0.5 g), ionic strength (0 and 10% NaNO₃), eluent volume (1 and 2 mL), eluent concentration (0.5 and 2 molL⁻¹), and desorption time (5 and 10 min) were the variables of interest in this experiment. The total design matrix showed 15 runs (12 + 3 center points) to be carried out randomly in order to eliminate the effects of extraneous or nuisance variables. The evaluation of the main effects was done based on ANOVA results and Pareto charts.

As it can be concluded from Figures 5 and 6, pH has significant positive effect on extraction recovery of Pb(II) and Cd(II). Also the results illustrated in Figures 5 and 6 confirm that eluent concentration and desorption time have significant positive effects on extraction recovery of Pb(II) and Cd(II), respectively. And other parameters show no significant effect on the extraction recovery of both elements.

Therefore, the Box-Behnken design (BBD) was performed to evaluate the optimum condition of performance of selective IL-FF-D-SPE of Pb(II) and Cd(II) for the three significant parameters: pH, eluent concentration, and desorption time. The 3D response surface plots for the extraction recovery (%) of both elements were shown in Figures 7 and 8. As seen in Figures

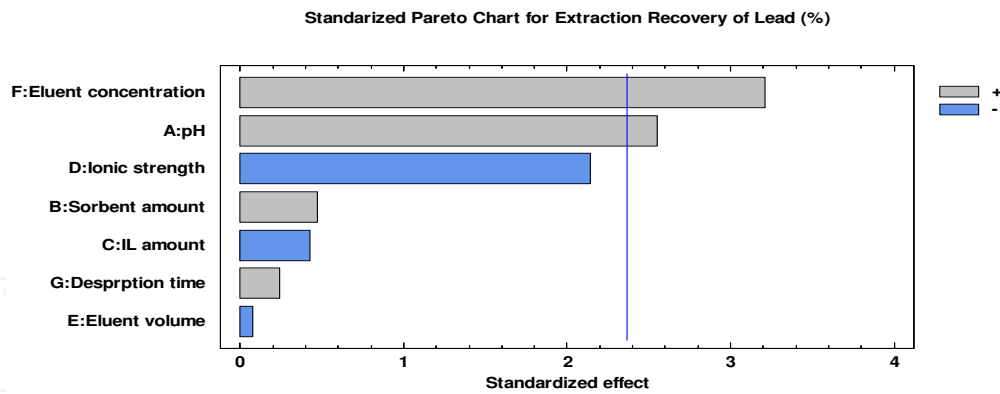


Figure 5. Standardized ($P = 0.05$) Pareto chart, representing the estimated effects of parameters obtained from the Plackett-Burman screening design for lead [14].

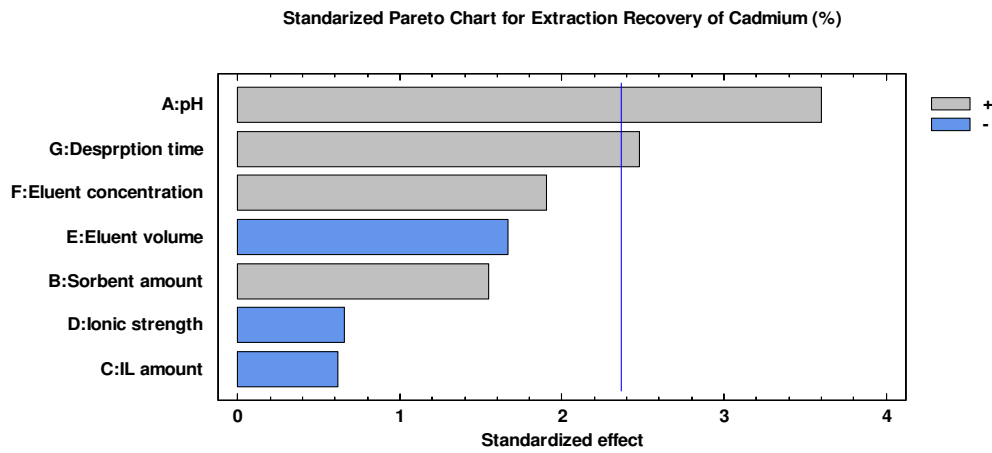


Figure 6. Standardized ($P = 0.05$) Pareto chart, representing the estimated effects of parameters obtained from the Plackett-Burman screening design for cadmium [14].

7 and 8, an optimization showed that the best pH is 6.7, eluent concentration of 1.59 molL^{-1} , and desorption time of 8 min.

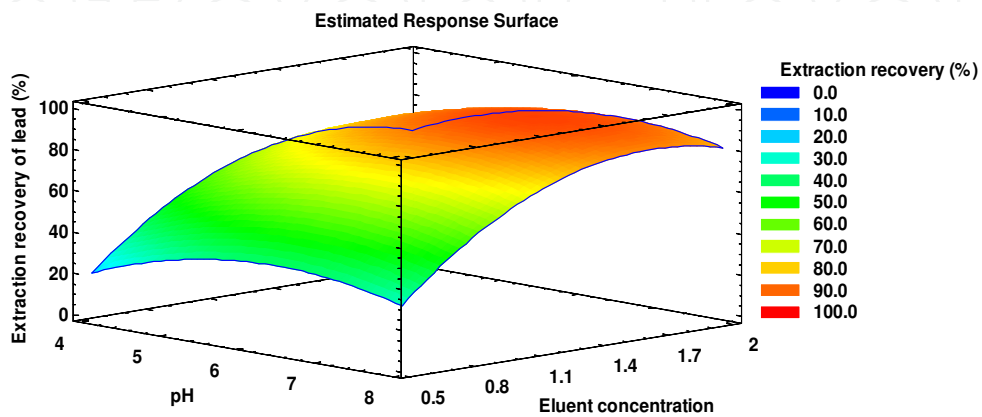


Figure 7. Estimated response surface by plotting extraction recovery (%) versus pH and eluent concentration [14].

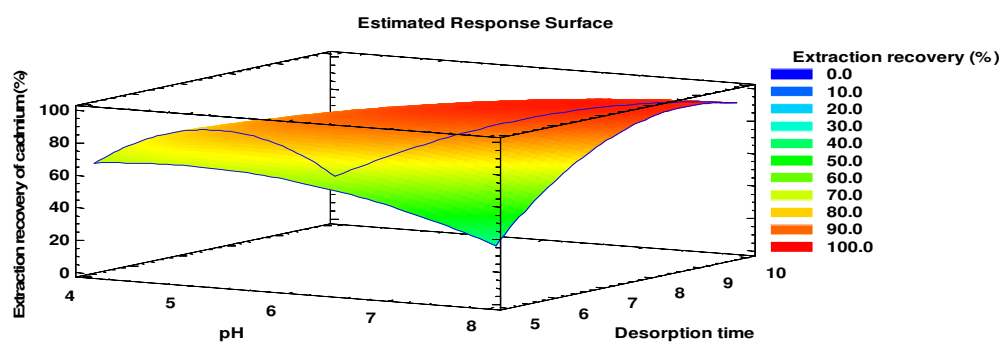


Figure 8. Estimated response surface by plotting extraction recovery (%) versus pH and desorption time [14].

3.3.4. Effect of potentially interfering ions

In order to assess the applications of the recommended procedure, the effect of potentially interfering ion on the extraction recoveries of Pb(II) and Cd(II) were also examined. For this purpose, by spiking appropriate amounts of potentially interfering ions in the range of 50-15000 $\mu\text{g mL}^{-1}$ to 50.0 mL of solution containing 40 $\mu\text{g L}^{-1}$ of Pb(II) and 30 $\mu\text{g L}^{-1}$ of Cd(II) evaluation was done. The obtained results were summarized in Table4.

Ions	Concentration ($\mu\text{g mL}^{-1}$)	Extraction recovery (%)	
		Pb(II)	Cd(II)
Na ⁺	15000	101.2 ± 2.4	98.8 ± 2.5
K ⁺	10000	97.8 ± 2.2	99.1 ± 2.5
Pd ²⁺	1000	96.9 ± 2.5	100.5 ± 2.6
Cu ²⁺	50	101.6 ± 2.4	101.3 ± 2.7
Ni ²⁺	100	98.4 ± 2.6	97.6 ± 2.4
Ag ⁺	50	98.9 ± 2.5	100.7 ± 2.6
Zn ²⁺	50	97.4 ± 2.3	96.9 ± 2.5
Mg ²⁺	500	99.2 ± 2.2	96.5 ± 2.4
Cl ⁻	10000	96.5 ± 2.3	97.2 ± 2.6
NO ₃ ⁻	15000	100.7 ± 2.4	98.4 ± 2.6

Table 4. Effect of coexisting ions on recovery of 40 $\mu\text{g L}^{-1}$ of Pb(II) and 30 $\mu\text{g L}^{-1}$ of Cd(II) (n = 3) [14].

3.3.5. Figures of merit and comparison of selective IL-FF-D-SPE with other methods

Under the optimum conditions, the relative standard deviations of 2.2 and 2.4 % were obtained for lead and cadmium, respectively (n = 7). The limit of detections were 1.21 $\mu\text{g L}^{-1}$ for Pb(II) and 0.21 $\mu\text{g L}^{-1}$ for Cd(II). The preconcentration factors were 250 for lead and 200 for cadmium and the maximum adsorption capacities of the sorbent were obtained 11.18 and 9.34 mg g^{-1} for lead and cadmium respectively.

The obtained results were compared with other literatures in Table 5. As it can be concluded from Table 5, in addition to selectivity of ionic liquid ferrofluid, the presented IL-FF-D-SPE method has lower limit of detection ($1.21 \mu\text{g L}^{-1}$ for lead and $0.21 \mu\text{g L}^{-1}$ for cadmium), higher preconcentration factor (250 and 200 for lead and cadmium respectively), good repeatability (RSD%) and sorption capacity.

Sorbent	PF/EF ^a		LOD ^b		RSD ^c (%)		Linear range ^d		Sorption capacity ^e		Ref.
	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	
Amberlite XAD-2 /PAN	50	50	23.2	0.8	4.1	2.9	0-3000	0-1000	1.35	2.56	[41]
Surfactant mediated Fe ₃ O ₄	25	25	0.74	0.15	3.82	3.15	1000-10000	100-1000	-	-	[42]
Chromosorb 101 / <i>Bacillus thuringiensis var.israelensis</i>	31	31	2.85	0.37	2.7	2.5	500-10000	20-2000	7.50	8.90	[44]
MWCN/tartrazine	40	40	6.6	0.8	-	-	500-8000	20-3000	-	-	[45]
Fe ₃ O ₄ /TiO ₂ /PAN	250	200	1.21	0.21	2.2	2.4	4-470	1-110	11.18	9.34	This work

^a Preconcentration factor or enrichment factor.

^b Limit of detection ($\mu\text{g L}^{-1}$).

^c Relative standard deviation.

^d ($\mu\text{g L}^{-1}$).

^e (mg g^{-1})

Table 5. Comparison of the proposed method with other SPE method used for preconcentration and FAAS determination of lead and cadmium ions [14].

3.3.6. Analysis of real samples

After digestion of milk, urine and blood plasma samples according to previous report [14], the standard addition method was applied for determination of trace amounts of Pb(II) and Cd(II) in these samples. The results are summarized in Table 6.

Sample	Pb(II)			Cd(II)		
	Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Milk ^a	0	ND ^b	-	0	ND	-
	10	10.2 ± 0.3	102.0	5	5.2 ± 0.2	104.0
	20	19.8 ± 0.5	99.0	15	14.6 ± 0.4	97.3
Urine	0	ND	-	0	ND	-
	10	10.4 ± 0.3	104.0	5	4.8 ± 0.2	96.0
	20	21.1 ± 0.6	105.5	15	15.3 ± 0.4	102.0
Blood Plasma plasma	0	ND	-	0	ND	-
	10	9.8 ± 0.3	98.0	5	5.2 ± 0.2	104.0

Sample	Pb(II)			Cd(II)		
	Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
	20	20.9 ± 0.6	104.5	15	15.1 ± 0.5	100.6

^a Pegah milk, Tehran, Iran.

^b Not detected

Table 6. Determination of Cd (II) and Pb(II) in real samples [14].

4. Conclusion and future work

Ionic liquids as environmentally friendly solvents with amazing properties such as negligible vapor pressure, low flammability, and liquid state in a broad temperature range can be used in sample preparation step such as D-LLE and also D-SPE, as mentioned in above studies. In term of D-LLE by choosing IL as extraction solvent, great improvement was achieved since only very small amount of the ionic liquid as a green extraction solvent was used as a replacement of environmentally damaging organic solvents in extraction procedure.

In addition, by introducing ionic liquid ferrofluids and also selective ionic liquid ferrofluid in to the field of sample preparation, great improvements were achieved. In order to simplicity and cost efficiency, in these environmentally friendly methods due to dispersion of sorbent in the aqueous phase, extraction is much faster in comparison with SPE which is time consuming column passing. Moreover, the magnetic separation greatly improved the separation rate. Therefore, no centrifugation is need for phase separation.

We believe that by combinations of ferrofluidic materials with appropriate chelators may lead to extraction schemes for various other ions. Typical combination may include ammonium pyrrolidine dithiocarbamate (APDC), 1-(2-thiazolylazo)-2-naphthol (TAN) and 1-Phenylthiosemicarbazide (1-PTSC) as chelate agents for complexation for Pb(II), Cd(II), Co(II) and Cu(II) or this method can be used in preconcentration of dyes without any need to chelate agents and determination by spectrophotometry methods. Finally, we hope in near future we all use the benefits of ionic liquids combined with these fast extraction methods.

Author details

Negin Fasih Ramandi and Farzaneh Shemirani*

*Address all correspondence to: shemiran@khayam.ut.ac.ir

Department of Analytical Chemistry, University College of Science, University of Tehran, Tehran, Iran

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