

Dispersive solid phase extraction of lead in environmental samples by Ionic liquid- based magnetic nanoparticle fluid

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ABSTRACT

For the first time the application of Ionic liquid-based magnetic nanoparticle fluid in dispersive solid phase extraction was investigated. As a result of using ionic liquid as dispersion medium, stability of colloidal magnetic dispersion against sedimentation improved. Due to rapid injection of an appropriate amount of ionic liquid-based magnetic nanoparticle fluid in to the aqueous sample by a syringe, extraction can be achieved within a few seconds. In addition, based on attraction of magnetic fluid to magnet, there is no need to centrifuge for phase separation. Determination of lead in different environmental samples was the purpose of this study. Therefore, the effect of different variables on the extraction yield was studied simultaneously using an experimental design. Under the optimized condition, the calibration graph was linear over the range of 5-372 ($\mu\text{g L}^{-1}$) and relative standard deviation of 1.34 % was obtained ($n = 7$). The limit of detection and enrichment factor (EF) was obtained 1.66 ($\mu\text{g L}^{-1}$) and 200 respectively.

1. INTRODUCTION

Toxic effects 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. 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 (Di Nezio 2004). The wide spread of lead throughout the environment is not limited to soil, surface water, or food; it is even found in polar snow (Adams 1998). Due to its toxicity, non- biodegradability, and tendency to accumulate in living organisms the regular absorption of small amounts 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 (Davudabadi Farahani 2013). Therefore, monitoring quantitative trace amount of lead in food, water and other environmental samples is imperative.

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Flame atomic absorption spectrometry (FAAS) is a widely used technique for quantification of metal species such as lead. However, low concentration and matrix interference occurring in real samples cause difficulty in the direct determination of this metal ion; therefore, preliminary preconcentration/separation procedures are required. Several enrichment procedures have been reported in the literature for lead determination involving different analytical techniques, such as cloud-point extraction (Cigdem 2013) precipitation (Shah 2013), liquid-liquid extraction (LLE) (Citak 2010), solid-phase extraction (SPE) (Tufekci 2013). In spite of some strength points, these methods suffer from some drawbacks. Therefore, some improvements are needed. In this study, we want to report very simple, fast and efficient preconcentration-separation method based on dispersive solid phase extraction which assisted by ionic liquid ferrofluid.

Magnetic nanoparticle fluid (Ferrofluids) consist of single- domain magnetic nanoparticles, which are dispersed in various fluids as carriers (Oliveira 2009). Therefore, they combine the basic properties of ferromagnetic nanoparticles and fluids at the same time. Typically, the amount of nanomagnetic compounds in ferrofluid is only a few percent which means that the concentration of magnetic particles is low; approximately 3-10%. Therefore, many properties of ferrofluid, such as: vapor pressure, density, pours point, and chemical properties are the same as the base fluid. In ferrofluid- based dispersive solid phase extraction, by using a syringe, an appropriate amount of ferrofluid is rapidly injected into the aqueous sample. Therefore, the sorbent is highly dispersed in aqueous phase and a large contact surface between the sample and the sorbent speeds up the mass transference processes and as a result, the extraction can be achieved within a few seconds. Extraction of lead in water samples was the purpose of this study and also by the help of chemometrics methods, experimental condition was optimized.

2.EXPERIMENTAL

2.1. Preparation of the ferrofluid

In order to prepare ferrofluid 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 tetra fluoro borate, [Hmim] BF₄. To obtain ferrofluid, the result suspension was sonicated for 30 min. The resulting suspension had a magnetite fraction of 9.1%.

2.2. Extraction

The sample, or standard solution containing Pb (II), 1-(2- pyridylazo)-2- naphtol (PAN) (4×10^{-7} mol.L⁻¹), NaNO₃ (3.78 w/v %), and buffer (pH=5.8) were poured into a 50 mL tube. Then, by using a 1.0 mL syringe, the ferrofluid was injected into the sample solution and a dark cloudy suspension was formed rapidly and the extraction process was quickly completed after approximately 10 seconds. Subsequently, a strong magnet was placed at the bottom of the tube to let the ferrofluid settle. After about 2 min, the solution became clear and limpid and supernatant was simply discarded by decanting it. After removing the

magnet, 1 mL nitric acid (2 mol.L^{-1}) was added to the vial to desorb the Pb(II) complex 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 FAAS.

3. RESULT AND DISCUSSION

3.1. Optimization

The effect of the following six factors were investigated by a half-fraction factorial design: pH (4 and 8), concentration of PAN (4×10^{-7} and $8 \times 10^{-6} \text{ mol L}^{-1}$), sorbent amount (0.01 and 0.03 gr), eluent volume (0.5 and 1 mL), extraction time (6 and 10 s), ionic strength (0 and 10%).

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. Based on obtained results, only pH and ionic strength have significant effects on extraction of lead. Therefore, in the next step these variables were optimized by central composite design. An optimization showed that the best pH is 5.8, and that the best extraction is achieved of the sample ionic strength is not larger than 3.78 (w/v %).

3.2. Figures of merit

Under the optimal experimental conditions, calibration curves were obtained for each metal ion by simultaneous preconcentrating of 50 mL of the sample solution. Table 1 features the analytical characteristics of the optimized method for extraction of lead, including: linear range, correlation coefficient, limit of detection (LOD) and reproducibility expressed as a relative standard deviation (RSD). A concentration factor (CF) of about 200 was obtained as a ratio between the volume of the sample solution and the final volume obtained after the elution step (1 mL).

Table 1: Analytical characteristics of the optimized method

Analyte	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Linear range ($\mu\text{g L}^{-1}$)	Preconcentration Factor
Lead	1.66	1.34	5-372	200

3.3. Analysis of real sample

Determination of lead in water samples was done based on using the standard addition method. The obtained result is summarized in Table 2.

Table 2:

Analytical result for determination of Pb(II) in water samples.

Sample	Spiked (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Mineral water ^a	0	ND ^e	-
	50	49.8 ± 1.2	99.6
	100	102.3 ± 1.9	102.3
Tap water ^b	0	ND	-
	50	51.8 ± 2.2	103.6
	100	103.1 ± 1.8	103.1

^a Zam zam mineral water, Iran.

^b From drinking water system of Tehran, Iran.

4. Conclusion

In the present study, the determination of traces of Pb(II) in water samples was investigated by ionic liquid ferrofluid based dispersive solid phase extraction (IL-FF-D-SPE). In addition to the simplicity of this method (in comparison to a solid phase extraction), it is also much faster due to dispersion of sorbent in the aqueous phase. 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. **The following key points in regards to IL-FF-D-SPE are considerably noteworthy:** simplicity, cost efficiency, and suitability for batch operations (which could greatly shorten the sample preparation time.)

REFERENCES

- Adams, F.C., Heisterkamp, M., Candelone, J.-P., LTURNUS, F., Van De Velde, K. and Boutron, C.F. (1998), "Speciation of organometal and organohalogen compounds in relation to global environmental pollution". *Analyst*. 123, 767- 772.
- Cigdem, Er., Filiz Senkal, B. and Yaman, M. (2013) "Determination of lead in milk and yoghurt samples by solid phase extraction using a novel aminothioazole-polymeric resin". *Food Chem*. 137, 55–61.

- Citak, D. and Tuzen, M. (2010) "A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry". *Food Chem. Toxicol.* 48, 1399-1404.
- Davudabadi Farahani, M. and Shemirani, F. (2013), "Ferofluid based dispersive-solid phase extraction for spectrophotometric determination of dyes". *J Colloid. Interf. Sci.* 407, 250-254.
- Di Nezio, M.S., Palomeque, M.E. and Fernandez Band, B.S. (2004), "A sensitive spectrophotometric method for lead determination by flow injection analysis with on-line preconcentration". *Talanta*, 63, 405- 409.
- Oliveira, F.C.C., Rossi, L.M., Jardim, R.F. and Rubim, J.C. (2009), "Magnetic fluids based on γ -Fe₂O₃ and CoFe₂O₄ nanoparticles dispersed in ionic liquids". *J. Phys. Chem. C*, 113(20), 8566-8572.
- Shah, F., Kazi, T.G., Ullah, N. and Afridi, H.I. (2013) "Determination of lead in biological samples of children with different physiological consequences using cloud point extraction method" *Biol. Trace Elem. Res.* 153,134-140.
- Tufekci, M., Bulut, V.N., Elvan, H., Ozdes, D., Soylak, M. and Duran, C. (2013) "Determination of Pb(II), Zn(II), Cd(II), and Co(II) ions by flame atomic absorption spectrometry in food and water samples after preconcentration by coprecipitation with Mo(VI)-diethyldithiocarbamate" *Environ. Monit. Assess.* 185, 1107–1115.