

Ionic liquid-based dispersive liquid-liquid microextraction for preconcentration of lead followed by high-performance liquid chromatographic determination

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Abstract. A new method was developed for the analysis of trace lead in water, using ionic liquid- based dispersive liquid-liquid microextraction (IL-DLLME) followed by high performance liquid chromatography with diode array detection (HPLC-DAD). 1,3-di(n-butyl)imidazolium hexafluorophosphate was used as the extraction solvent. Various parameters that affect extraction efficiency were investigated, and the optimized experimental conditions were obtained. The analytical performance of the method was evaluated under the optimum conditions, the limit of detection (LOD) was 0.15µg/L and the RSD was 4.6 %. The proposed method was applied to the determination of lead in various water samples with recoveries in the range of 95.5-104.0 %.

1. Introduction

Heavy metals have aroused considerable concerns [1]. Lead is a typical toxic heavy metal element, which tends to be accumulated in human vital organs and thus cause serious health problems [2]. Air, water and soil may be contaminated by lead. Therefore, it is essential to develop sensitive and reliable analytical techniques for the analysis of lead in various environmental matrices. Inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry can perform sensitive determination of heavy metals [3-7]. However, they need expensive instrumentation.

Because lead in environmental water samples is often at low levels, a sample preparation step is usually required before its determination. Among various preconcentration and separation techniques for metal ion and organic pollutants, solid phase extraction is the most frequently used one [8-14]. Recently, dispersive liquid-liquid microextraction (DLLME) as a simple, fast, sensitive, low-cost and solvent-less microextraction technique has been developed [15-18].

Ionic liquids (ILs) have recently been employed as alternatives to conventional toxic chlorinated solvents. The most commonly used ionic liquids for extraction are those with cations based on imidazolium or pyridinium ring [19, 20]. Because of their negligible vapor pressure, high thermal stability and good solubility for organic and inorganic compounds, ILs has been utilized in many fields including environmental analysis [21-23].

In this study, we present a novel method for analysis of trace Pb(II) in aqueous samples, based on a DLLME with HPLC-DAD. Dithizone (DZ) acted as the chelator for Pb(II). The experimental conditions were investigated and optimized. Finally, the developed method was applied to the determination of Pb(II) in different water samples.



2. Materials and methods

2.1 Reagents

1-Hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆], 99%) was purchased from Aladdin Reagent (Shanghai) Co., Ltd (Shanghai, China). Dithizone (80.0%) was obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Hydrochloric acid and nitric acid were of ultra purity grade, other reagents were of analytical reagent grade.

2.2 Instruments

The separation and analysis were performed on a HPLC system (SHIMADZU, Kyoto, Japan) equipped with a diode-array detection (DAD, SPD-M20A). A Shim-pack VP-ODS column (150 × 4.6 mm I.D.) was used.

2.3 Dispersive liquid–liquid microextraction procedures

A mixture of 50 µL of [HMIM][PF₆] (extraction solvent) and 0.6 mL of methanol (disperser solvent) was quickly injected into a sample solution. After 5 min the cloudy solution was centrifuged. The dispersive droplets of [HMIM][PF₆] were sedimented at the bottom of centrifuge tube. 20µL of which was injected into the HPLC system using a microsyringe.

3. Results and discussion

3.1 Effect of sample pH

The effect of sample pH was studied in the range of 5-10. Fig.3 shows the dependence of extraction recovery of Pb(II) on sample pH value. As can be seen, this effect was significant. The recovery enhanced with the enhancement of pH from 5 to 8. Satisfactory recovery for Pb(II) was achieved in the pH range of 8-9. The decrease in extraction of Pb(II) at low pHs may due to competition of H⁺ with Pb(II) for reaction with DZ. When pH value was larger than 10, the recovery dropped. Thus, pH 8.0 was selected.

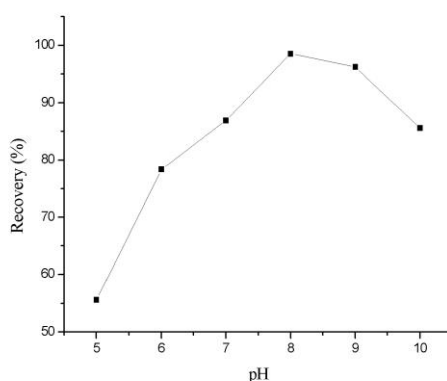


Fig.1 Effect of sample pH.

3.2 Effect of DZ concentration

The effect of dithizone concentration on the preconcentration efficiency for lead was investigated in a range from 0.0002 to 0.001 % (w/v), and the results are shown in Fig.2. It is obvious that the extraction recovery for Pb(II) enhanced with the increase of dithizone concentration from 0.0002 to 0.0006 %, and then kept almost unchanged up to 0.001 %. Based on these results, 0.0006 % (w/v) was employed as the optimal DZ concentration.

3.3 Effect of extraction solvent volume

To examine the effect of [HMIM][PF₆] volume on the extraction efficiency, the volume of [HMIM][PF₆] was adjusted in the range of 30–70 μ L. As can be seen in Fig.3, the extraction efficiency increased with increasing the volume of [HMIM][PF₆] from 30 to 50 μ L. However, the extraction efficiency decreased when the volume was larger than 50 μ L. Therefore, 50 μ L was chosen as the optimal extraction solvent volume.

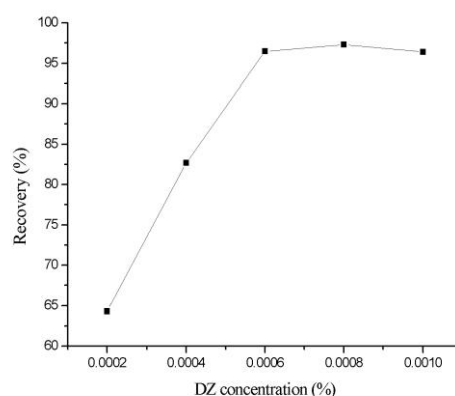


Fig.2 Effect of DZ concentration.

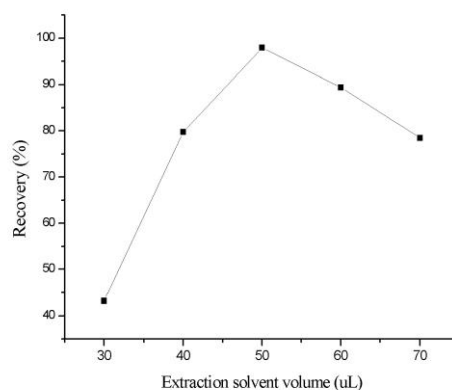


Fig.3 Effect of extraction solvent volume.

3.4 Effect of disperser solvent volume

In this work, methanol was used as the disperser solvent. To examine the effect of methanol amount on the extraction recovery of Pb(II), different volumes of methanol (0.2, 0.4, 0.6, 0.8 and 1.0 mL) were tested. The results showed that the extraction recovery increased by increasing the volume of methanol up to 0.6 mL and then decreased with further increasing of methanol volume. Hence, 0.6 mL of methanol was chosen for further investigation.

3.5 Analytical performance

Under the optimized conditions mentioned above, the analytical performance of the proposed method was evaluated. It was found that in a Pb(II) concentration range of 1–50 μ g/L, good linear correlation coefficient could be obtained ($R^2=0.9962$). The limit of detection (LOD) were 0.15 μ g/L. The relative standard deviation (RSD) for five replicate measurements of 5.0 μ g/L Pb(II) was 4.6%.

3.6. Water samples analysis

The proposed technique was applied to the determination of trace amount of Pb(II) in three water samples, and the analytical results were given in Table 1. As can be seen, the recovery for the spiked samples was between 95.5% and 104.0%, and the RSD for Pb(II) concentration in the real samples ranged from 3.1 to 5.4%.

Table 1 Analytical results of Pb(II) in water samples.

Sample	Pb add/($\mu\text{g/L}$)	Pb found/($\mu\text{g/L}$)*	Recovery/%	RSD(%)
Lake water	0	15.6	---	4.1
	20.0	34.7	95.5	4.4
River water	0	52.4	---	3.6
	50.0	98.5	96.1	3.1
Pond water	0	8.9	---	5.4
	10.0	19.3	104.0	4.9

4. Conclusions

The present study described a new method, DLLME coupled with HPLC-DAD, for trace lead analysis. The proposed method was proved to be fast, sensitive, precise and easy to operate, and was applied to the extraction and analysis of Pb(II) ions in real water samples with satisfactory analytical results.

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