

# Preconcentration of Copper and Lead Using Deep Eutectic Solvent Modified Magnetic Nanoparticles and Determination by Inductively Coupled Plasma Optical Emission Spectrometry

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Received: Dec. 17, 2019; Revised: Jan. 16, 2020; Accepted: Feb. 3, 2020; Published: Feb. 25, 2020.

**ABSTRACT:** In this work, an efficient and eco-friendly magnetic solid-phase extraction method was developed for the simultaneous preconcentration and separation of copper and lead from environmental samples. Deep eutectic solvent modified nano-Fe<sub>3</sub>O<sub>4</sub> particles (Fe<sub>3</sub>O<sub>4</sub>-DES) were used as the adsorbent in the MSPE procedure. The analytes were trapped by the adsorbent while stirring and separated from the solution by the action of an external magnetic field. Then, the analytes were eluted from the surface of Fe<sub>3</sub>O<sub>4</sub>-DES with HNO<sub>3</sub> solution and determined by inductively coupled

plasma optical emission spectrometry (ICP-OES). Several factors affecting the extraction efficiency, such as type of DES, pH of the solution, extraction time, amount of the adsorbent, sample volume, and the volume and concentration of the eluent, were investigated. Under the optimal conditions, the detection limits of the proposed method were 0.29  $\mu$ g L<sup>-1</sup> and 0.51  $\mu$ g L<sup>-1</sup> for copper and lead respectively, with a relative standard deviation of 3.55% and 2.62%, respectively (n=7). Verification of the accuracy of the method was carried out by analysis of certified reference materials. The method was applied to the determination of trace amounts of copper and lead in environmental samples with satisfactory results.



# INTRODUCTION

In recent years, pollution of the environment with heavy metals has received considerable attention because it poses a great threat to human health and environmental safety. Some toxic elements such as lead (Pb) are considered extremely dangerous even at trace levels. Pb can affect almost all organs and systems in the human body, which includes blood enzyme changes, hyperactivity, and neurological disorders.<sup>1,2</sup> There are also some metal elements that have different physiological effects depending on their concentration. Copper (Cu), for instance, is an essential element for all biological systems at low concentrations and is involved in the formation of some enzymes and the connective tissue, for maintaining the health of the central nervous system, immune function, and hormone secretion. But at high concentrations, some of these metals can contribute to the deterioration of the human body, especially for children.<sup>3,4</sup> As a result, the determination of the

concentration of metal ions in environmental samples is of utmost importance in order to help assess the state of the eco-system.

However, the direct determination of trace heavy metal ions in environmental samples is often difficult due to matrix effects and insufficient sensitivity of the instrumental methods. In order to achieve accurate and reliable analytical results, an efficient sample pretreatment procedure is often required. The most widely used techniques for the separation and preconcentration of trace Cu and Pb includes solid-phase extraction,<sup>5,6</sup> cloud point extraction,<sup>7,8</sup> liquid-phase <sup>9,10</sup> or dispersion liquid-liquid microextraction.<sup>11-13</sup> Magnetic solid-phase extraction (MSPE) is a relatively new mode of the SPE method, and offers simpler operation, uses no organic solvents, and has a high preconcentration factor.<sup>14,15</sup> The magnetic adsorbent combines with the analyte during the extraction process, and then simply separates from the matrix by an external magnetic field. This MSPE separation process requires no centrifugation, filtration, or column packing operation.

The most common magnetic material in MSPE are the nano-Fe<sub>3</sub>O<sub>4</sub> particles, which have an ultra-high specific surface area, are super paramagnetic, and low cost.<sup>16</sup> However, in many cases, nano-Fe<sub>3</sub>O<sub>4</sub> particles do not have sufficient affinity or selectivity for the analytes. Many organic modifiers are modified on the surface of the nano-Fe<sub>3</sub>O<sub>4</sub> particles to enhance the affinity and selectivity between the adsorbent and the analytes, but most of them are harmful to the operator and do not conform to the concept of green chemistry.<sup>17,18</sup> To overcome this problem, ionic liquids have recently been used in MSPE because of their low toxicity relative to conventional organic solvents.<sup>19,20</sup> But the complicated synthesis step is difficult to biodegrade and expensive due to the use of ionic liquids, which limits their application.

Recently, deep eutectic solvents (DES) have received

more and more attention because of their unique physical and chemical properties. They are considered to be an liquids alternative to ionic and have similar (negligible physicochemical properties volatility. non-flammability, and stability).<sup>21,22</sup> As a new eco-friendly solvent, DES has various additional advantages such as biodegradability, low toxicity, high atomic utilization, low cost, and simple preparation. These solvents are synthesized by simply mixing a hydrogen bond donor (HBD), such as alcohol, carboxylic acids and amines, with a hydrogen bond acceptor (HBA), such as quaternary salt. In addition, the melting point of DES is lower than for any of the individual components because of the formation of intermolecular hydrogen bonds.<sup>23,24</sup> DES can form unique interactions with target compounds ( $\pi$ - $\pi$ , hydrogen bonding, or anion exchange), and has the great potential as a green solvent for the extraction of different analytes, including proteins, organic pollutants, and metal ions.<sup>25-28</sup>

In this study, the nano-Fe<sub>3</sub>O<sub>4</sub> particles modified with DES (Fe<sub>3</sub>O<sub>4</sub>-DES) were synthesized for the MSPE separation and preconcentration of Cu and Pb. Systematic optimization of the conditions affecting the extraction efficiency was carried out to obtain optimal performance of the MSPE procedure. The proposed method was applied to the determination of trace amounts of Cu and Pb in environmental samples.

## EXPERIMENTAL

**Apparatus.** An iCAP 6300 inductively coupled plasma optical emission spectrometer (Thermo Fisher, USA) was used for the Cu and Pd determinations. The operating conditions are summarized in Table 1. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China), equipped with a glass combination electrode. A model XH-800C microwave digestion system (Beijing Xianghu

Table 1. ICP-OES operating conditions

Parameters	Values
RF power (W)	1150
Plasma gas (Ar) flow rate (L min <sup>-1</sup> )	12
Auxiliary gas (Ar) flow rate (L min <sup>-1</sup> )	1.0
Nebulizer gas (Ar) flow rate (L min <sup>-1</sup> )	0.57
Integration time (s)	3
Solution pump rate (rpm)	50
Wavelength (nm)	Cu 324.754, Pb 220.353

Science and Technology Development Co. Ltd., Beijing, China) was used to dissolve the solid samples. A neodymium-iron-boron ( $Nd_2Fe_{12}B$ ) magnet was used for phase separation.

Standard solution and reagents. The stock standard solutions (1000 mg L<sup>-1</sup>) of Cu and Pb were purchased from Macklin (Shanghai, China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Nano-Fe<sub>3</sub>O<sub>4</sub> (purity >99.0%, 20 nm spherical powder) was purchased from Aladdin (Shanghai, P. R. China). Choline chloride (ChCl >98%) was supplied by 9-Ding Chemistry (Shanghai, China). Urea, ethylene glycol (EG), oxalic acid (OX), and Glycerol (VG) were provided by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All reagents were of analytical reagent grade. Deionized water was produced using the Arium® ultrapure water system (Sartorius Stedim Biotech, Gottingen, Germany). All containers were kept in 10% nitric acid for at least 24 hours and washed four times with deionized water before use.

**Preparation of Fe\_3O\_4-DES.** The DESs employed in this study were a combination of a certain molar ratio of chloride with HBD, including urea, ethylene glycol, oxalic acid, and glycerol. The DESs were prepared by stirring the mixtures at 80 °C until a homogeneous and clear liquid was formed. To modify the nano-Fe<sub>3</sub>O<sub>4</sub> particles with DES, 100 mg nano-Fe<sub>3</sub>O<sub>4</sub> was added to 10 mL of DES, and the mixture was thoroughly stirred to a homogenous solution for 20 minutes. The resulting material was washed successively with methanol and deionized water, then heated to 60 °C for 4 h in an oven. According to the results of elemental analysis, the content (m/m) of C in the adsorbent was 0.159%, N was 0.134%, and H was 0.056%. The mass of the DES, modified with the nano-Fe<sub>3</sub>O<sub>4</sub> particles, was calculated as 5.0 mg g<sup>-1</sup>.

General procedure. Aliquots of 50.0 mL sample solutions containing 0.5  $\mu$ g mL<sup>-1</sup> Cu<sup>2+</sup> and Pb<sup>2+</sup> were adjusted to a specific pH and placed into 100-mL beakers. Then, 30 mg of Fe<sub>3</sub>O<sub>4</sub>-DES was added, and the solution stirred vigorously for 10 min to facilitate the adsorption of the metal ions into the adsorbent. The adsorbent at the bottom of the beaker was collected with an external magnet, and the supernatants were decanted directly. After washing with deionized water, 0.5 mL of 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> was added as the eluent and shaken for 5 min. Above metal ions in the eluent were determined by ICP-OES.

Sample preparation. Two environmental certified reference materials (GBW07307 stream sediments and GBW07405 soil, obtained from the Perambulation Institute of Physical Geography and Geochemistry of Geological and Mineral Ministry, Langfang, P.R. China) were used to verify the accuracy of the developed method. All samples were dried in an oven at 60 °C. A portion (0.1 g) of the dried samples was accurately weighed into a PTFE vessel, treated with 2 mL of HF, 6 mL of concentrated HNO<sub>3</sub>, and 3 mL of H<sub>2</sub>O<sub>2</sub>. The digestion procedures were set as follows: (1) temperature 130 °C for 10 min, (2) 150 °C for 5 min, (3) 180 °C for 5 min, (4) 210 °C for 15 min. The solution was heated to near dryness and the residue dissolved in 0.1 mol  $L^{-1}$  of HNO<sub>3</sub>. The final volume was made up to 100 mL volume with deionized water. A lake water was collected from the East Lake (Wuhan), and a tap water was collected from our laboratory. All samples were filtered through a 0.45 µm membrane filter and analyzed as soon as possible. A soil sample was obtained from the grounds on our campus.

## **RESULTS AND DISCUSSION**

Selection of type of DES. In this work, the hydrophilic DES adsorbent was modified on the surface of the nano-Fe<sub>3</sub>O<sub>4</sub> particles. As a part of the adsorbent that directly interacts with the metal ions, the type of DES has a significant effect on the extraction efficiency. Therefore, the optimization experiments of the DES, formed with different types of HBD with ChCl in various molar ratios, were carried out. These HBD candidates contained -NH, -OH, -COOH, respectively, capable of forming DES with ChCl and remaining liquid at room temperature. As shown in Fig. 1, when the DES was formed with ChCl-urea at the ratio of 1:2, the recoveries for Cu<sup>2+</sup> and Pb<sup>2+</sup> were highest. Thus, this DES ratio was selected as optimal for further experiments.

**Optimization of adsorption conditions.** The optimization conditions, such as solution pH, extraction time, amount of adsorbent, and sample volume affecting the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  into Fe<sub>3</sub>O<sub>4</sub>-DESe, were studied to achieve optimal performance of the MSPE method. In order to simplify this process, the desorption operation was not performed at this stage, and the metal ions in the supernatants were directly determined by ICP-OES after the extraction. To evaluate the adsorption efficiency, the recovery was calculated as  $(C_i-C_s)/C_i \times 100\%$ , where  $C_i$  was the concentration of the metal ions in the supernatants after the extraction.

It is well known that the pH of the solution plays an important role in the MSPE of metal ions. The pH not only affects the interaction between the adsorbent and the metal ions, but also influences the solubility of the nano-Fe<sub>3</sub>O<sub>4</sub> particles in the solution. The effect of pH of the solution on the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> was studied in the range from 3.5 to 6.5, and the results are shown in Fig. 2a. It was found that the recoveries of Cu<sup>2+</sup> and Pb<sup>2+</sup> increased rapidly with an increase in the pH from 3.5 to 5.5, and no significant increase was observed



Fig. 1 Effect of DES type on the extraction efficiency.



**Fig. 2** Optimization of adsorption conditions. (a) pH of solution; (b) extraction time; (c) amount of sorbent; (d) sample volume.

when the pH exceeded 5.5. Therefore, pH 5.5 was applied for subsequent experiments.

In the MSPE procedure, the time allotted for extraction must be sufficient to trap the metal ions into the adsorbent. The effect of extraction time was examined in the range from 2 to 15 min using the same experimental conditions. As shown in Fig. 2b, an equilibration time of 8 min was required for the quantitative extraction of the metal ions into the adsorbent. Thus, the equilibrium time of 10 min was selected in subsequent experiments.

The effect of the amount of adsorbent was tested in the range from 10 to 40 mg. As shown in Fig. 2c, quantitative extraction of  $Cu^{2+}$  and  $Pb^{2+}$  was achieved by using 30 mg

of Fe<sub>3</sub>O<sub>4</sub>-DES. At higher amounts of the adsorbent, the extraction efficiency was almost constant. The sample volume is one of the important parameters influencing the preconcentration factor (PF). Therefore, the effect of sample volume on the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> was investigated. For this purpose, 30 mg of Fe<sub>3</sub>O<sub>4</sub>-DES was added to solutions with volumes ranging from 50 to 200 mL and containing 2.5  $\mu$ g of Cu<sup>2+</sup> and Pb<sup>2+</sup>. All solutions were submitted to the extraction procedure using the optimal conditions. The obtained results (Fig. 2d) demonstrates that for the simultaneous extraction of Cu<sup>2+</sup> and Pb<sup>2+</sup>, the dilution effect for a sample volume up to 100 mL was not significant. Subsequent experiments were carried out using 50 mL of sample solution.

**Optimization of elution conditions.** As can be seen in Fig. 2a, the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  at pH<3 was negligible. Therefore, a HNO<sub>3</sub> solution was used to elute the trapped metal ions from the adsorbent. Fig. 3 shows that 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> is sufficient to elute  $Cu^{2+}$  and  $Pb^{2+}$  simultaneously. The effect of eluent volume on the recoveries of  $Cu^{2+}$  and  $Pb^{2+}$  was also studied. In our experiment, a quantitative elution was obtained with use of 0.5 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub>.

Adsorption capacity. The adsorption capacity (AC) is another important parameter for the MSPE method, because it determines how much adsorbent is required to quantitatively concentrate the analytes from a given solution. To evaluate the factor, 50 mL of each metal ion solution at 20  $\mu$ g mL<sup>-1</sup> was used to perform the recommended procedure, and the maximum AC was calculated. The AC of Fe<sub>3</sub>O<sub>4</sub>-DES for Cu and Pb was found to be 21.7 mg g<sup>-1</sup> and 31.4 mg g<sup>-1</sup>, respectively.

Table 3.	Comparison	with the	published	methods
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Fig 3. Effect of concentration of the eluent.

Table 2. Effect of the coexisting ions concentration on targets

Ion	Coexisting	Coexisting	Recovery (%)		
	ion/Cu <sup>2+</sup>	ion/Pb <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	
NO <sub>3</sub>	27000	27000	101	95.8	
$Na^+$	10000	10000	101	95.8	
$\mathbf{K}^{+}$	10000	10000	95.1	97.8	
$\mathbf{NH_4}^+$	10000	10000	106	97.7	
$Mg^{2+}$	1000	1000	106	98.9	
Ni <sup>2+</sup>	200	1000	96.3	98.0	
Zn <sup>2+</sup>	100	1000	96.1	97.8	
Ca <sup>2+</sup>	100	1000	95.3	95.2	
Fe <sup>3+</sup>	100	100	101	97.1	
Hg <sup>2+</sup>	100	100	98.0	98.8	
C0 <sup>2+</sup>	100	100	98.3	96.7	
Mn <sup>2+</sup>	100	100	95.3	97.8	
Al <sup>3+</sup>	50	50	94.1	96.2	

Effect of interferences. The effect of common coexisting ions on the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  on Fe<sub>3</sub>O<sub>4</sub>-DES was investigated. In these experiments, solutions of 0.1 µg mL<sup>-1</sup> of Cu<sup>2+</sup> and Pb<sup>2+</sup> containing the interfering ions were treated according to the recommended procedure, and the results are summarized in Table 2. Under the optimal conditions, the presence of major cations and anions has no significant influence on the preconcentration of Cu<sup>2+</sup> and Pb<sup>2+</sup>.

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Methods	Line curve range (µg L <sup>-1</sup> )		LOD (µg L <sup>-1</sup> )		EF		A (mg	C (g <sup>-1</sup> )	References
	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	—
SPE	3-100	5-100	0.30	2.60	160	160	1.92	1.94	Dadfarnia et al.29
SPE	3-400	8-500	0.80	1.80	120	120	13.0	18.0	Dalali et al. <sup>30</sup>
MSPE	/	2-250	/	1.10	/	100	/	25.0	Karimi et al.31
MSPE	/	5-330	/	1.61	/	200	/	10.5	Farahani et al.32
MSPE	1-600	1.7-1000	0.29	0.50	192	198	21.7	31.4	This work

Table 4. Results of Cu and Pb in CRMs (µg g<sup>-1</sup>, n=5)

Samples	Elements	Found	Certified value
GBW07307	Cu	38±2	38.6±2.7
stream sediments	Pb	350±26	336.8±12.8
CDW07405 soil	Cu	166±9	158.6±4.5
GD W0/403 8011	Pb	552±44	561.2±10.5

Table 5. Results of Cu and Pb in real samples (µg L<sup>-1</sup>, n=5)

Samplas	Addad	For	Recovery (%)		
Samples	Audeu	Cu	Pb	Cu	Pb
Lake water	0	5.3±0.4	8.5±0.1	/	/
	10	14.7±0.6	18.1±0.4	94	96
	100	$100.8 \pm 1.2$	$107.8 \pm 1.3$	95.5	99.3
Tap water	0	1.3±0.3	2.0±0.4	/	/
	10	11.0±0.6	11.5±0.4	97	95
	100	97.1±1.2	97.3±2.6	95.8	95.3
Soil	0	24.1±1.0	13.8±0.5	/	/
	100	123.3±1.7	114.1±6.8	96.7	102.1
	200	224.5±2.1	213.1±2.7	102	94.9

Characteristics of the method. The performance of proposed method was investigated using optimal conditions. The calibration curves were obtained for the determination of Cu and Pb according to the general procedure. Linearity was maintained at 1.0-600 µg L<sup>-1</sup> for Cu and 1.7-1000 µg L<sup>-1</sup> for Pb. The coefficient of determination (r<sup>2</sup>) was 0.999 for Cu and 0.999 for Pb. The limit of detection was found to be 0.29  $\mu$ g L<sup>-1</sup> and 0.50  $\mu$ g L<sup>-1</sup> for Cu and Pb, respectively. The intra-day relative standard deviation (RSD, n=7) of the method was 3.55% for Cu and 2.62 % for Pb. The inter-day RSD was obtained by testing the adsorbents prepared for the same batch for seven consecutive days, and the results were 4.23% and 3.02% for Cu and Pb, respectively. According to the equation of the enrichment factor (EF) =  $C_e/C_i$ , where C<sub>i</sub> is the concentration of the metal ions in the initial solution and Ce is the concentration of the metal ions in the eluents. The calculated EF for Cu was 192 and for Pb was 198 when the maximum sample volume of 100 mL was used.

**Comparison with the reported methods.** A comparison of the proposed method with reported SPE or MSPE methods are summarized in Table 3. Our proposed method has a wider linear range and better LOD than that of the most methods, which due to the excellent

adsorption capacity of the adsorbent. In addition, the present method has a higher EF than the other methods, which is an important evaluation parameter for SPE.

**Analytical application.** In order to establish the validity of the proposed procedure, the method was applied to the determination of Cu and Pb in environmental certified reference materials (CRMs) (GBW07307 stream sediments and GBW07405 soil). The analytical results are given in Table 4. As can be seen, the determined values were in good agreement with the certified values despite the complicated matrices of these samples. The proposed method was applied to the determination of Cu and Pb in lake water, tap water, and real soil samples. In addition, the recovery experiments of different amounts of Cu and Pb were carried out, and the results are listed in Table 5. The results indicate that the recoveries are reasonable for trace analysis, in the range of 94–102.1%.

#### CONCLUSIONS

In this work, a stable, convenient, high capacity sorbent was developed and successfully applied to the MSPE method. The experimental procedure is simple and easy to operate. In particular, there is no organic solvent used throughout the experimental. Due to the excellent sorption capacity of the developed adsorbent, the proposed method has the advantages of wide linear range, lower LOD, and good precision. In addition, the satisfactory results obtained for several real samples analyzed demonstrate the feasibility of this method for environmental samples.

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#### Notes

The authors declare no competing financial interest.

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