Magnetic Dispersive Micro-solid Phase Extraction of Ni(II) and Pb(II) on ZnFe₂O₄ Nanotubes for Their Determination by Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Due to the rapid development of industry and agriculture, pollution of heavy metals has attracted world-wide attention. Heavy metal ions have long half-lives and are difficult to be degraded. What is more, they easily accumulate in living organisms, and most of them are known to be highly toxic (1, 2). Exposure to lead (Pb) can affect the human nervous and immune system, and harm the brain, heart, kidneys, stomach, and lungs (3). Nickel (Ni) is an essential element for humans at trace level. However, if ingested in excess amounts, Ni can cause dermatitis, pulmonary fibrosis degeneration, cardiovascular and renal diseases (4). Therefore, it is of great importance to develop new methods for the determination of these heavy metal ions in environmental and biological samples (5-8).

Currently, various techniques have been used for the determination of metal ions in real samples, including atomic absorption spectrometry, anodic stripping voltammetry, atomic fluorescence spectrometry, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), and neutron activation analysis (9-17). However, the direct determination of trace elements in real samples without preconcentration and

ABSTRACT

Magnetic ZnFe₂O₄ nanotubes (ZFONTs) were prepared as a new adsorbent for dispersive micro-solid phase extraction of Ni(II) and Pb(II) in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry. The adsorption behaviors of the target ions on ZFONTs were studied. The results indicated that the analytes were quantitatively retained on ZFONTs in the pH range of 6.0–8.0, and eluted completely with 1.0 mL of 0.3 mol L⁻¹ HNO₃ solution. Separation of the sorbent from the aqueous phase was achieved by an external magnet to avoid tedious centrifugation or filtration steps. The main parameters influencing preconcentration and determination of the analytes were studied in detail. Under the optimum conditions, the detection limits of this method were 0.39 and 2.1 pg mL⁻¹ for Ni and Pb, respectively. The relative standard deviations were less than 6.0% (n=9, c=1.0 ng mL⁻¹). This method was used for the determination of trace Ni(II) and Pb(II) in water samples and a certified reference material of bovine liver with satisfactory results. The recoveries for the spiked samples were in the range of 94.0–105%.

separation by these techniques is generally restricted due to the extremely low concentrations of the analytes and complex matrix interferences. To achieve accurate and sensitive results, a sample pretreatment step is usually required before determination (18-20). As a classical sample pretreatment technique, solid phase extraction (SPE) is a preferred technique for the analysis of an element and its speciation because of its advantages such as simple operation, lower cost, higher enrichment factor, and the ability to combine with different detection techniques (21-25). However, this technique suffers from certain shortcomings, including solvent loss, large secondary wastes, and a long procedure (26). In addition, a liquid sample is passed through a column containing an adsorbent in conventional SPE. Small-size adsorbents such as nanoparticles can escape from the SPE column and can cause high pressure in the SPE system.

In order to solve the problems mentioned above, many researchers have focused on developing simplified and miniaturized sample pretreatment methods. Among them, dispersive micro-solid phase extraction (DMSPE) as a new sample preparation technique has received increasing attention. Compared with traditional SPE, DMSPE can offer many benefits of reduced solvent consumption, less adsorbent usage, short extraction time, and high extraction efficiency (27-30). It is worth noting that the adsor-

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bent material plays a very important role in DMSPE. Therefore, the development of a new adsorbent material is forever of interest to analysts.

Over the last few years, various nanometer-size materials have attracted substantial interest in the analytical sciences due to their excellent characteristics (31-37). Among them, magnetic nanoparticles have shown great potential as adsorbents because of their smaller particle size, large surface area, high adsorption activity, and magnetic property. Some magnetic nanomaterials have been employed for the preconcentration and separation of inorganic and organic substances in DMSPE (38-43). Magnetic ZnFe_2O_4 nanotubes (ZFONTs) not only possess tubular structure, but also exhibit many pores on their wall. The specific surface area of ZFONTs is much bigger than that of ZnFeO_4 nanoparticles (44). In comparison with magnetic carboxyl-modified nanodiamonds, ZFONTs have a higher preconcentration factor (45). Moreover, ZFONTs are polar, unlike some mesoporous carbon materials (46), and can highly disperse in water, which leads to more contact between adsorbent and analytes. These facts reveal to us that ZFONTs may have a great analytical potential as an adsorbent in DMSPE. To the best of our knowledge, however, the study on this topic has received little attention so far.

In this work, ZFONTs were investigated as an adsorbent in DMSPE for the preconcentration and determination of trace/ultra-trace Ni(II) and Pb(II) by ICP-MS. The adsorption behaviors of the target ions on ZFONTs were investigated systematically. The experimental parameters affecting preconcentration, separation and determination of the analytes were examined in detail. On the basis of the experimental results obtained,

a novel method of DMSPE with ZFONTs coupled to ICP-MS was developed for the simultaneous determination of trace Ni(II) and Pb(II) in environmental and biological samples.

EXPERIMENTAL

Instrumentation

An X-7 Series ICP-MS system (Thermo Fisher Scientific, USA) was used in this work. The instrumental operating conditions for ICP-MS are listed in Table I. A pH meter with a combined electrode was used to control the pH values of the solutions (Thermo Fisher Scientific, USA). The mixture was sonicated using a KQ-50E ultrasonic bath (Kunshan Ultrasonic Instrument Co., Ltd., Suzhou, P.R. China). Sample digestion was performed by an Ethos T microwave digestion device (Milestone, Italy). A strong neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{12}\text{B}$) magnet was used for phase separation. The surface morphology of the ZFONTs was characterized by scanning electron microscopy (SEM) (MAIA 3 LMH, TESCAN, Czech Republic).

Reagents and Standard Solutions

All reagents used in this experiment were of analytical grade and

purchased from Shanghai Reagent Factory (Shanghai, P.R. China). Stock solutions of Ni and Pb (1.0 mg mL^{-1}) were obtained from the National Analysis Center of Iron & Steel (Beijing, P.R. China). Working solutions were prepared by step-wise dilution of the above stock solutions just before use. High purity deionized water was obtained from a Milli-Q[®] A10 system (Millipore Corporation, USA) and used during this work. All glassware and plastics were soaked in $2.0 \text{ mol L}^{-1} \text{ HNO}_3$ solution overnight, and cleaned with deionized water before use. Synthesis of the ZFONTs was carried out in our laboratory according to the literature (47).

Dispersive Micro-solid Phase Extraction

An aliquot of a 20-mL sample solution containing target ions was placed into a 50-mL test tube. A 20-mg amount of the ZFONTs was added to the test tube. The pH of the sample was adjusted to about 7.0 with HNO_3 or NaOH solution. Then, the mixture of the sorbent and sample was sonicated with a vortex for 50 seconds to facilitate dispersion of the ZFONTs in the sample. After extraction, a strong magnet was placed at the bottom of the test tube to separate the

TABLE I
ICP-MS Operating Parameters

Plasma Power	1.3 kW
Plasma Argon Flow Rate	14 L min^{-1}
Auxiliary Argon Flow Rate	0.87 L min^{-1}
Nebulizer Argon Flow Rate	0.91 L min^{-1}
Sampler Orifice (nickel)	1.1 mm
Skimmer Orifice (nickel)	0.7 mm
Acquisition Mode	Peak-jumping
Number of Sweep	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotope	^{60}Ni and ^{208}Pb

ZFONTs from the aqueous solution. Subsequently, the aqueous phase was discarded, and the ZFONTs remained in the test tube. To desorb the analytes, 1.0 mL of 0.3 mol L⁻¹ HNO₃ solution was added to the test tube containing the ZFONTs, and the test tube was ultra-sonicated for 40 seconds. Finally, the sorbent was separated with the magnet, and the analytes in the solution were determined by ICP-MS.

Sample Preparation

A sample portion of 0.0100 g GBW(E) 080193 Bovine Liver, provided by National Research Center for Geo-analysis, Beijing, P.R. China, was accurately weighed into a 100-mL Teflon[®] vessel, then 3.0 mL concentrated HNO₃ and 1.0 mL H₂O₂ were added, respectively. After about 5 minutes, the digestion vessels were closed and placed into a microwave oven. Then, the samples were digested in the microwave oven at 180 °C (ramp, 10 minutes; hold, 15 minutes) and 1 kW power. After cooling, the solution was transferred into a Teflon[®] beaker, and heated to near dryness on a hot plate. The residues were dissolved with 0.1 mol L⁻¹ HNO₃ solution and diluted to a desired volume.

Water samples (collected from Wuhan, P.R. China) were filtered

immediately through a 0.45-μm membrane filter, acidified to about pH 2.5 with concentrated HNO₃, and then kept at 4 °C before use. The blanks were prepared exactly as the samples except without addition of analytes.

RESULTS AND DISCUSSION

Characterization of ZFONTs

The surface morphology of the ZFONTs was examined by SEM with EDS. Figure 1 shows that the ZFONTs possess a mean outer diameter of about 258 nm, and have many nanopores on their wall which consist of the ZnFeO₄ nanoparticles. Moreover, the hollow structure of ZFONTs can be watched from the transection image, and their mean inner diameter is approximately 150 nm. These facts suggest that the ZFONTs with tubular structure and many nanopores on their wall have a large specific surface area, and may become a great adsorbent.

Effect of Sample pH

In DMSPE, the pH of the aqueous solution is an important variable that controls the adsorption of the analytes on the ZFONTs as it affects the existing form of the analytes and the surface charge of the

sorbent. Therefore, the effect of pH on the adsorption of the analytes was investigated in the pH range of 1.0–8.0. It can be seen from Figure 2 that the adsorption percentage of the analytes increases with an increasing pH of the sample solution, and their quantitative recoveries (>90%) were obtained in the pH range of 6.0–8.0. Therefore, a pH of about 7.0 was used for subsequent experiments. The low recoveries of the analytes in the range of pH 1.0–5.0 may be explained in terms of surface charge of the ZFONTs. At an acidic condition, the surface of ZFONTs is electropositive, which repels the cations (Ni²⁺ and Pb²⁺).

Influence of Adsorbent Amount

To establish the optimum amount of sorbent necessary for the separation and preconcentration of the analytes, different dosages of the ZFONTs were tested from 5 to 40 mg per sample solution (20 mL). The results show that satisfactory recoveries (>90%) of the analytes were obtained using amounts of ZFONTs ranging from 20–40 mg (Figure 3). Thus, 20 mg ZFONTs were used in this work.

Selection of Extraction Time

For DMSPE, mass transfer takes place during the dispersive step.

Fig. 1. Images of ZFONTs by scanning electron microscopy.

Fig. 2. Effect of pH on recoveries of analytes using ZFONTs as adsorbent.

The effect of sonication time was evaluated in the range of 5–80 seconds. The results in Figure 4 indicate that the recoveries of the analytes increased within the first 40 seconds, and then the recoveries of the analytes remained approximately constant after exceeding 40 seconds. Hence, a sonication time of 50 seconds was selected for further study.

Selection of Eluent Parameters

Owing to the low adsorption efficiency of the analytes at pH < 1.0, a diluted HNO₃ solution was used for their quantitative desorption from the ZFONTs by vortex. The effect of HNO₃ concentration on the recoveries of the analytes was studied in the concentration range of 0.1–0.5 mol L⁻¹. The experimental results show that the analytes were quantitatively eluted within the concentration range of 0.3–0.5 mol L⁻¹ HNO₃ solution (Table II).

The effect of eluent volume on the adsorption of the analytes was also examined using 0.5, 1.0, 1.5, and 2.0 mL of 0.3 mol L⁻¹ HNO₃, respectively. The results indicated that the quantitative recoveries (>90.0%) were obtained with 1.0 mL of 0.3 mol L⁻¹ HNO₃ solution. In addition, the effect of elu-

tion time on the recoveries of the analytes was evaluated in the range of 5–60 seconds by vortex. The results showed that 40 seconds was sufficient for the quantitative desorption of the analytes from the sorbent. Finally, 1.0 mL of 0.3 mol L⁻¹ HNO₃ with an elution time of 40 seconds was employed as the optimum elution condition.

Effect of Sample Volume

One of the important aspects for DMSPE development is to explore its capability of extracting analytes at very low concentration levels from a large volume of real samples. Hence, the effect of sample volume on the extraction of the analytes was investigated by different sample volumes ranging from 10–150 mL containing 5.0 ng of the target

ions. The results in Table III show that 120 mL is the largest sample volume at which quantitative extraction of the analytes is achieved. However, the recovery of the analytes decreased with a further increase in sample volume. Because the elution volume was 1.0 mL, an enrichment factor of 120 was obtained. In this work, a sample volume of 20 mL was used for routine analysis.

Effect of Coexisting Substances

To evaluate the application potential of this method, the different concentrations of interfering ions were individually added to the sample solution containing 3.0 ng mL⁻¹ of the analytes, and their effects on the recoveries of the ana-

TABLE II
Effect of Eluent Concentration on Recoveries of Analytes

Eluent (HNO ₃ , mol L ⁻¹)	% Recovery Ni ²⁺	% Recovery Pb ²⁺
0.1	73.1	78.3
0.2	82.7	85.6
0.3	96.5	97.2
0.4	98.3	95.1
0.5	94.7	99.2

TABLE III
Effect of Sample Volume on Recoveries of Analytes

Sample Volume (mL)	% Recovery Ni ²⁺	% Recovery Pb ²⁺
10	96.1	98.4
40	98.7	96.1
80	97.2	94.6
100	95.3	97.2
120	93.7	95.7
150	81.2	84.6

Fig. 3. Effect of adsorbent dose on recoveries of analytes.

Fig. 4. Effect of extraction time on recoveries of analytes using ZFONTs as adsorbent.

lytes were investigated under the optimum conditions. The tolerance limit of coexisting ions is defined as the largest amount making the variation less than 10% in the recovery of the analytes. The results in Table IV indicate that this method has satisfactory matrix resistance capability.

Adsorption Capacity

Adsorption capacity is a useful parameter for assessing an adsorbent and depends on its nature. In this work, the adsorption capacity of the analytes on the ZFONTs was measured using the procedure in the literature (48). 20-mL aliquots of the sample solutions containing the analytes in the concentration range of 10–30 $\mu\text{g mL}^{-1}$ were pre-concentrated and eluted under the selected conditions. The amount of the analytes adsorbed on the ZFONTs (mg g^{-1}) at each concentration level was determined by this method. Breakthrough curves were plotted by the concentration of the analytes versus their amount adsorbed on per gram of the adsorbent (Figure 5). The adsorption capacities for Ni(II) and Pb(II), calculated from the breakthrough curves, were 26.7 and 23.1 mg g^{-1} , respectively. It is worth mentioning that the ZFONTs have higher adsorption capacities for Ni(II) and Pb(II) than those reported in the literature (49, 50).

TABLE IV
Effect of Coexisting Ions on Recoveries of Analytes

Coexisting Ions	Concentration ^a (mg L^{-1})
Na^+ , K^+	5000
Ca^{2+} , Mg^{2+}	2000
Fe^{3+} , Al^{3+}	5.0
Cu^{2+} , Zn^{2+} , Cd^{2+}	300
SO_4^{2-} , CO_3^{2-} , PO_4^{3-}	2000
Cl^- and NO_3^-	5000

^a Recovery > 90%.

Analytical Features

The important parameters of this method, including precision, detection limits, and linear range of the calibration curve, were validated under the optimized conditions. The instrumental detection limits, based on three times the standard deviation of 10 measurements of a reagent blank, were 46.8 and 252 pg mL^{-1} for Ni and Pb, respectively. The detection limits of this method were calculated by dividing the instrumental detection limit by the pre-concentration factor (120), resulting in 0.39 and 2.1 pg mL^{-1} , respectively (51). The high extraction efficiency of the analytes on the ZFONTs enhances the sensitivity of this method. The calibration curves were observed as the linear

and the concentrations range from 0.5 pg mL^{-1} to 5000 pg mL^{-1} for the analytes with a correlation coefficient better than 0.9981. Relative standard deviations (RSD) for the analysis of 10 replicate measurements of a 20-mL standard solution containing 1.0 ng mL^{-1} Ni(II) and Pb(II) were 5.7% and 4.8%, respectively.

Application of Method

The accuracy of this method was examined by the determination of Ni(II) and Pb(II) in water samples. The reliability was checked by spiking the sample. The results along with the recovery for the spiked sample are given in Table V. The recoveries for the spiked samples were in the range of 94.0–105%.

Fig. 5. Breakthrough curves of analytes on ZFONTs.

TABLE V
Analytical Results and Recoveries of Analytes in Water Samples

Sample	Element	Added (ng mL^{-1})	Found ^a (ng mL^{-1})	Recovery (%)
Lake Water	Ni(II)	0	1.31 ± 0.10	-
		1.0	2.34 ± 0.12	103
	Pb(II)	0	1.98 ± 0.15	-
		1.0	2.95 ± 0.17	97.0
River Water	Ni(II)	0	0.73 ± 0.06	-
		1.0	1.78 ± 0.11	105
	Pb(II)	0	1.21 ± 0.07	-
		1.0	2.15 ± 0.13	94.0

^a Mean value $\pm$ Standard deviation, $n=5$.

In order to validate this method further, a certified reference material of GBW(E) 080193 Bovine Liver was also analyzed. The student's *t*-test (at $p < 0.05$) was applied to the obtained and the certified results (52). It can be seen from Table VI that there is no significant difference between the obtained results and the certified values of the samples.

CONCLUSION

In this work, magnetic ZFONTs were used as an adsorbent in DMSPE for the preconcentration and determination of Ni(II) and Pb(II) by ICP-MS. The adsorption behaviors of the target ions on the ZFONTs were examined in detail. The analytes were quantitatively adsorbed in the pH range of 6.0–8.0, and diluted completely with 1.0 mL of 0.3 mol L⁻¹ HNO₃ solution. An enrichment factor of 120 was obtained in this study. The separation of the magnetic sorbent from the aqueous phase was achieved by an external magnet. The use of the magnetic separation greatly improved the sample treatment time. Additionally, this method has the merits such as high tolerance limits of diverse ions and low detection limit. This study reveals the potential application of magnetic ZFONTs with tubular structure and many nanopores on their walls for preconcentration, separation and determination of trace/ultra-trace heavy metals and their speciation in real samples.

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TABLE VI
Analytical Results of Analytes in CRM GBW(E) 080193 Bovine Liver

Element	Added ($\mu\text{g g}^{-1}$)	Found ^a ($\mu\text{g g}^{-1}$)	Certified ^b ($\mu\text{g g}^{-1}$)	Recovery (%)
Ni(II)	0	0.26 $\pm$ 0.02	0.28	-
	0.5	0.75 $\pm$ 0.04	-	98.0
Pb(II)	0	0.57 $\pm$ 0.03	0.54	-
	0.5	1.10 $\pm$ 0.06	-	106

^a Mean value $\pm$ standard deviation, $n=5$.

^b Reference value.

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