



# Zincon-immobilized silica-coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles for solid-phase extraction and determination of trace lead in natural and drinking waters by graphite furnace atomic absorption spectrometry

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## ABSTRACT

A new protocol using zincon-immobilized silica-coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Zincon-Si-MNPs) as solid-phase extraction (SPE) medium has been developed for the separation and preconcentration of trace lead in water. Various parameters such as pH, extraction time, concentration and volume of eluent, sample volume, and influence of co-existing ions have been investigated in order to establish the optimum conditions for the determination of lead in combination with graphite furnace atomic absorption spectrometry (GFAAS). The detection limit (LOD) of the proposed method for lead based on an enrichment factor of 200 was 10 ng L<sup>-1</sup>. The relative standard deviations (RSDs, *n* = 5) were 8.3%, 7.8% and 9.2%, respectively, at 5, 0.5 and 0.05 ng mL<sup>-1</sup> levels. This method has been successfully applied to the analysis of trace lead in natural and drinking water samples and the recoveries for the spiked samples were in the range of 84–104%.

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## 1. Introduction

Lead is classified as prevalent toxic metal, which constitutes a major environmental health problem. Because lead and their compounds are widely used as chemical materials in modern society, they are widespread in environmental waters. Therefore, the development of fast, sensitive and reliable analytical methods to assess lead in water samples is an important topic. Several analytical methods including inductively coupled plasma optical emission spectrometry (ICP-OES) [1–3], inductively coupled plasma-mass spectrometry (ICP-MS) [4,5], flame atomic absorption spectrometry (FAAS) [6–9] and graphite furnace atomic absorp-

tion spectrometry (GFAAS) [10,11] have been proposed for the determination of lead in various matrices. However, the direct determination of lead in real samples with above techniques in most cases was very difficult because of matrix effect and low existing level. Therefore, a separation and/or preconcentration step was always required before analysis. Solid-phase extraction (SPE) technique is known as such kind of sample pretreatment method and it has become more and more popular due to its high enrichment factor, simple operation, minimal cost, reusability of the adsorbent and easy automation [12]. In SPE procedure, the choice of a proper adsorbent is the key to achieve full recovery, high enrichment factor, good selectivity, large capacity and fast extraction [13]. Up to date, a variety of adsorbents, such as functionalized silica gel [14], modified and unmodified active carbon [15,16], modified foam [17] and nanometer-sized material [18–20] have been extensively employed for the enrichment of lead. Among these materials, silica gel was the most common one owing to the advantages of mechanical, thermal and chemical stability under various conditions [12]. In order to improve the selectivity, silica gel was always modified by attaching organic and inorganic molecules to its surface [13]. However, these conventional media usually possess comparatively low adsorption capacity and long extraction time especially when dealing with large sample volume, so the continuous quest for novel high performance adsorbents is the objective of numerous analysts.

**Abbreviations:** Zincon-Si-MNPs, zincon-immobilized silica-coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles; SPE, solid-phase extraction; GFAAS, graphite furnace atomic absorption spectrometry; LOD, limit of detection; RSD, relative standard deviation; ICP-OES, inductively coupled plasma optical emission spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; FAAS, flame atomic absorption spectrometry; FI-IR, Fourier transform infrared spectrometer; TEM, transmission electron microscope; XRD, X-ray diffraction; TEOS, tetraethoxysilane; MNPs, magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles; Si-MNPs, silica-coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles; SAED, selected area electron diffraction.

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Nanometer-sized materials are the just kind of new adsorbents and have gained much attention because of their distinct chemical, physical and biological properties [21]. They are meant to be clusters of atoms or molecules of metal and oxide, ranging in size from 1 nm to almost 100 nm, and falling between single atoms or molecules and bulk materials. Most of atoms stand on the surface of nanometer-sized particle. These unsaturated surface atoms possess highly chemical activity and are prone to binding with other atoms [22]. In other words, nanometer materials are able to adsorb metal ions with high adsorption capacity. They have been widely applied in organic compounds analysis [23] and inorganic ions analysis [24]. As a special kind of nanometer-sized materials, magnetic nanoparticles have magnetic property besides the general characteristics of nanometer-sized materials and have obtained extensive applications in cell labeling [25], drug delivery [26], targeted imaging and therapy [27] during the past few years. Recently, they have also been used as adsorbents in SPE for environmental pollutant analysis [28]. In the magnetic SPE process, magnetic nanoparticles served as adsorbent are added into sample solution firstly, and then analytes are tagged with magnetic particles and can be removed from large volume samples using a magnet. After that analytes are desorbed from magnetic particles by small volume eluent and determined through different analytical instrumentation. Compared with non magnetic SPE, magnetic SPE have the following advantages: The adsorbent needs not be packed into the cartridge when using dynamic extraction mode, and no centrifugation or filtration of sample is needed after extraction when static batch mode is applied. Their separation and concentration are easier, more convenient and faster than other SPE methods. Hu et al. [29] employed magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles as adsorption material for the removal of Cr(VI) from wastewater, and the adsorption capacity was proved to be very high.

However, it should be noted that naked inorganic nanoparticles are inclined to aggregate, and are not selective and suitable for the samples with complex matrix [30]. Hence, the surface modification of these magnetic nanoparticles with a specific ligand has been proven to be a selective, quick, simple and efficient way. There have been only a few reports on the use of magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles modified with different reagents such as  $\gamma$ -mercaptopropyltrimethoxysilane [31], bismuthiol-II [32], 2-amino-5-mercapto-1,3,4-thiadiazole [33] and decanoic acid [34] for the separation and concentration of metal ions. In this present work, a novel adsorbent named zincon-immobilized silica-coated magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles has been for the first time prepared and employed for the extraction and determination of trace lead in natural and drinking waters.

## 2. Experimental

### 2.1. Apparatus

A Hitachi Z-2000 atomic absorption spectrometer (Hitachi, Tokyo, Japan) equipped with a heated graphite tube atomizer was employed for the determination of lead. A Pb hollow cathode lamp (Hitachi) operated at 6.5 mA was utilized as the radiation source. Measurements were carried out in the integrated absorbance (peak area) mode at 283.3 nm, using a spectral band width of 1.3 nm. The heated program applied for lead determination is given in Table 1.

The pH values were controlled by a Mettler Toledo 320-S pH meter (Mettler-Toledo, Shanghai, China) supplied with a combined electrode. A KQ3200DE ultrasonic bath with temperature control (Kunshan Shumei Ultrasonic Instrument, Suzhou, China) was used to disperse the nanoparticles in solution. An Nd-Fe-B magnet (8.0 mm  $\times$  6.0 mm  $\times$  1.6 mm) was used for magnetic

**Table 1**

The temperature program of graphite furnace atomizer.

Step	Start T/°C	End T/°C	Ramp time/s	Hold time/s
Drying	80	140	40	0
Ashing	500	500	20	0
Atomizing	1400	1400	0	5
Clean	2200	2200	0	4
Cool	0	0	0	9

separation. The zincon-immobilized silica-coated magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were characterized by TENSOR27 Fourier transform infrared spectrometer (FT-IR) (Bruker, Ettlingen, Germany) and JEM-200CX high-resolution transmission electron microscope (HRTEM) (JEOL, Tokyo, Japan). The samples for TEM were obtained by drying sample droplets from water dispersion onto a 300-mesh Cu grid coated with a lacey carbon film, which was then allowed to dry prior to imaging. The X-ray diffraction (XRD) spectra were collected on an ARL X'TRA diffractometer with Cu  $K\alpha$  radiation (ARL, Lausanne, Switzerland).

### 2.2. Standard solution and reagents

The stock standard solution for Pb (1000 mg L<sup>-1</sup>) was supplied by China National Measuring Science Research Institute (Beijing, China). Standard solutions were prepared by appropriate dilution of the stock solutions daily. Analytical grade or electronic pure reagents were used unless otherwise specified. Highly pure deionized water (18.2 M $\Omega$  cm) obtained from a Labconco system (Labconco, Kansas City, MO, USA) was used throughout this work. Plastic and glass containers and all other immersed laboratory materials that could come into contact with samples or standards were stored in 20% (v/v) nitric acid, and rinsed with highly pure deionized water prior to use. Zincon was purchased from First Reagent Factory (Shanghai, China). Tetraethoxysilane (TEOS) was obtained from Aladdin's reagent network (Aladdin, Shanghai, China).

Certified Reference Material of Environment Water (GBW08607) was supplied by China National Measuring Science Research Institute (Beijing, China).

Yibao mineral spring water, Jingtian mineral spring water and Wahaha purified drinking water were bought from local supermarkets in Nanjing, China. Tap water was drawn from the local supply system in Nanjing, China.

### 2.3. Preparation of zincon-immobilized silica-coated magnetic $\text{Fe}_3\text{O}_4$ nanoparticles

#### 2.3.1. Magnetic $\text{Fe}_3\text{O}_4$ nanoparticles (MNPs)

The preparation of MNPs was based on an improved chemical co-precipitation method described by Huang [35]. Briefly,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (11.68 g) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (4.30 g) were dissolved in 200 mL deionized water under nitrogen atmosphere with vigorous stirring at 85 °C. Then, 20 mL of 30% aqueous ammonia was injected into the mixture rapidly and the color of bulk solution changed from orange to black immediately. After magnetically separated via an external magnetic field, MNPs was washed twice with deionized water and ethanol respectively. And finally MNPs was dried under vacuum at 70 °C.

#### 2.3.2. Silica-coated magnetic $\text{Fe}_3\text{O}_4$ nanoparticles (Si-MNPs)

MNPs were dispersed in the mixture solution with tetraethoxysilane (TEOS, 10% (v/v), 80 mL) and propanetriol (60 mL) in a 250 mL round-bottom flask. The pH of the suspension was adjusted to 4.5 using glacial acetic acid, and subsequently, the mixture was stirred and heated at 90 °C for 2 h under a nitrogen

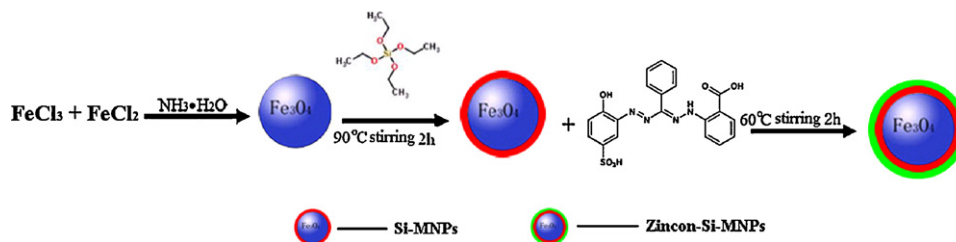


Fig. 1. Procedure for synthesizing zircon-immobilized silica-coated magnetic nanoparticles.

atmosphere. After cooled to room temperature, Si-MNPs was magnetically separated and washed sequentially with ethanol and deionized water three times respectively, and then dried under vacuum at 70 °C.

### 2.3.3. Zincon-immobilized silica-coated magnetic $Fe_3O_4$ nanoparticles (Zincon-Si-MNPs)

Si-MNPs were dispersed in 150 mL of 0.1% zircon in 95% ethanol and the pH of the suspension was adjusted to 4.5 using glacial acetic acid. The mixture was transferred to a 250 mL 3-necked round-bottom flask and then stirred and heated at 60 °C for 2 h under a nitrogen atmosphere. After magnetic separation, the Zincon-Si-MNPs were washed with deionized water and ethanol three times respectively, and finally dried under vacuum at 70 °C. Fig. 1 shows the synthesis procedure for Zincon-Si-MNPs.

### 2.4. Procedure of magnetic solid phase extraction

10 mL of aqueous sample solution were transferred into a glass beaker, and the solution pH was adjusted to 6.5 with 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O if necessary. 20 mg of Zincon-Si-MNPs was subsequently placed into the solution. The mixture was ultrasonicated for 2 min and magnetically separated via an external magnetic field. Then 0.5 mL 1 mol L<sup>-1</sup> HCl was added into the beaker as eluent and the new mixture was ultrasonicated again for 2 min. Finally, the adsorbent was removed via an external magnetic field and the supernatant was collected for the determination of Pb by GFAAS. Highly pure deionized water was chosen as the blank solution and subjected to magnetic SPE as described above. The

magnetic SPE process is illustrated in Fig. 2. The whole magnetic SPE procedure and GFAAS determination were performed in triplicate.

## 3. Results and discussion

### 3.1. Characterization of Zincon-Si-MNPs

#### 3.1.1. FT-IR spectrum

To confirm that zircon was bonded to the surface of MNPs, the characterization was performed by FT-IR spectroscopy. The FT-IR spectra for MNPs, Zincon-Si-MNPs and zircon are shown in Fig. 3. For MNPs, the peak at 562 cm<sup>-1</sup> was related to Fe–O group. Compared with naked MNPs, the vibration of Fe–O group in Zincon-Si-MNPs was shifted to 586 cm<sup>-1</sup>. The absorbance around 1086 cm<sup>-1</sup> observed in the curves Zincon-Si-MNPs (B) and zircon (C) corresponded to C–O stretching vibration. Moreover, the peak of 1500 cm<sup>-1</sup> found in the spectra of Zincon-Si-MNPs and zircon was assigned to skeletal vibration of benzene ring. The above results indicated that the zircon has been already coated to the surface of MNPs successfully.

#### 3.1.2. TEM images

In order to get direct information on particle size and morphology, the typical TEM micrographs for MNPs and Zincon-Si-MNPs are shown in Fig. 4. It can be seen that the diameter of MNPs (Fig. 4A) was about 10 nm, while the average diameter of Zincon-Si-MNPs (Fig. 4B) was 15 nm. By the comparison of the selected area electron diffraction (SAED) patterns of MNPs (Fig. 4C) and Zincon-Si-MNPs

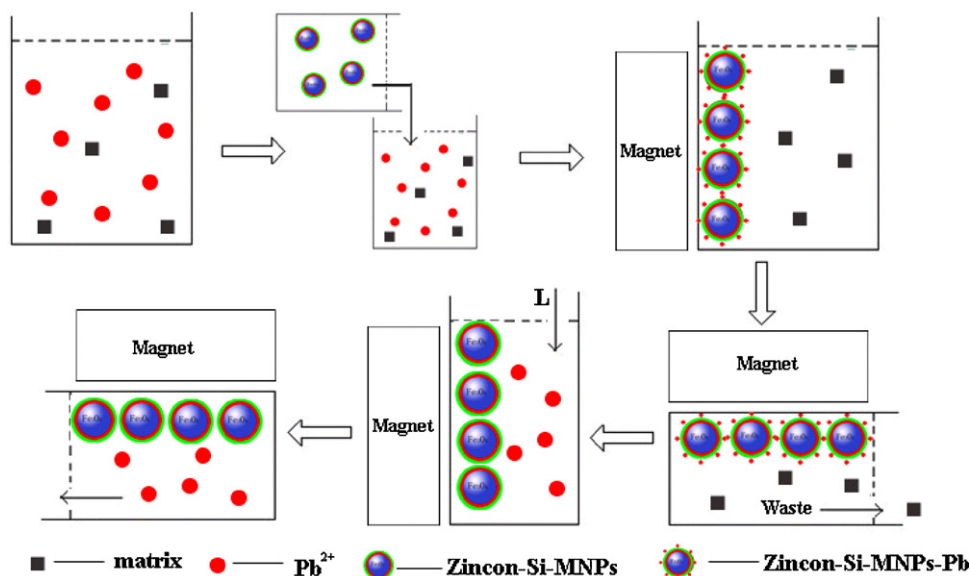


Fig. 2. Procedure for magnetic solid phase extraction.

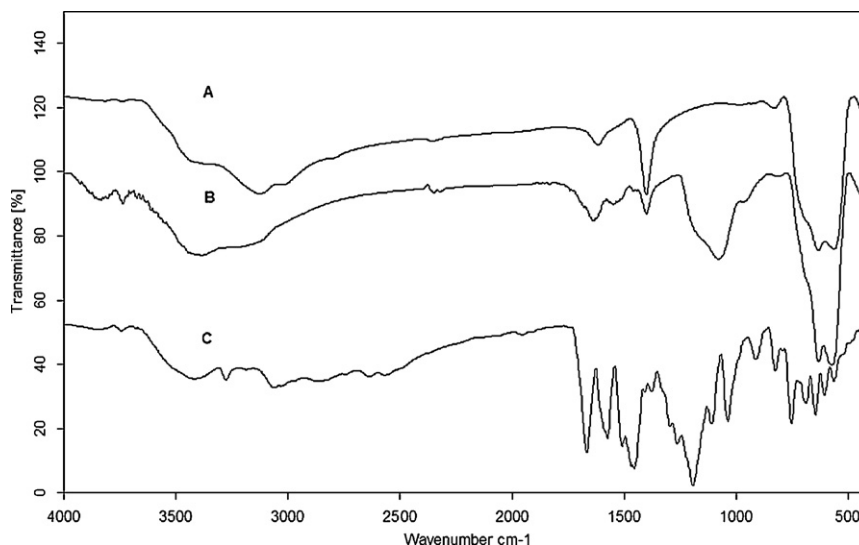


Fig. 3. IR spectra of MNPs (A), Zincon-Si-MNPs (B) and zincon (C).

(Fig. 4D), the weak outer diffraction rings of the cubic structure observed in Fig. 4D indicated the amorphous silica of the Zincon-Si-MNPs.

### 3.1.3. XRD pattern

The structures of synthesized MNPs and Zincon-Si-MNPs were analyzed by XRD and the results are showed in Fig. 5. The six characteristic peaks occurred at  $2\theta$  region of  $20\text{--}70^\circ$  were marked by their corresponding indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) respectively, which match well with the standard XRD data cards of  $\text{Fe}_3\text{O}_4$  crystal (JCPDS No. 19-06290).

### 3.2. Optimization of magnetic SPE parameters

The extraction procedure of Zincon-Si-MNPs for Pb was optimized using Pb standard solution. Lead in the supernatant after the first magnetic separation was determined by GFAAS to check the adsorption efficiency of Zincon-Si-MNPs for Pb every time.

#### 3.2.1. Effect of pH

pH value plays a very important role in view of the adsorption of Pb on Zincon-Si-MNPs. The effect of pH on the recovery of Pb is illustrated in Fig. 6. The recovery of Pb was nearly zero during pH range of 1–3 and then improved with the increase of pH

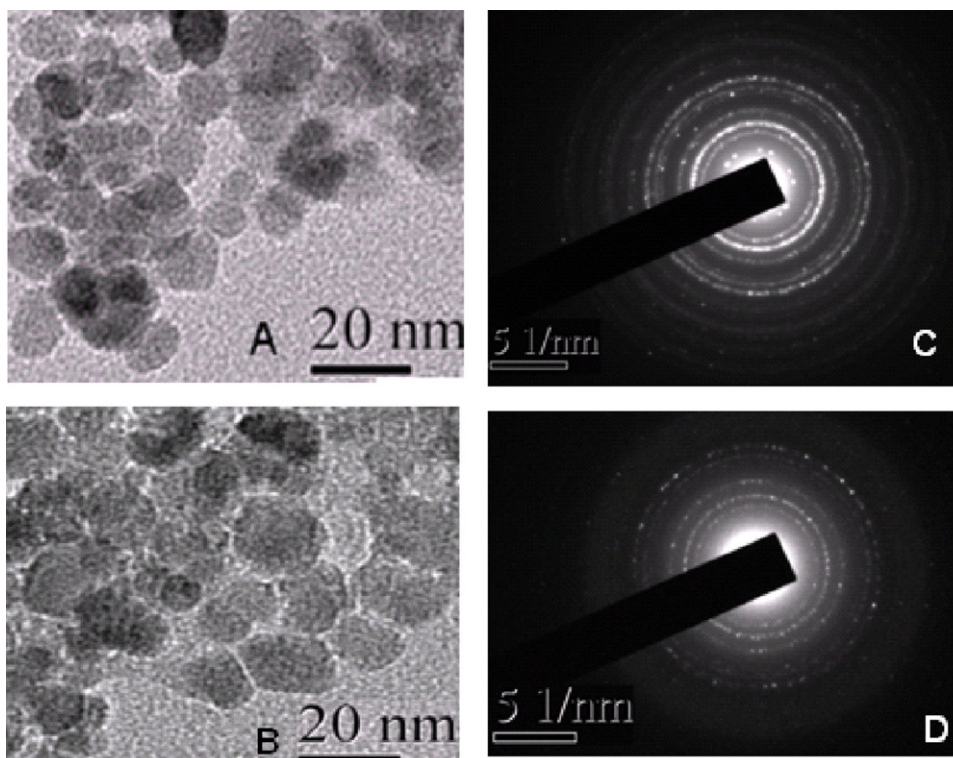


Fig. 4. TEM images of MNPs (A) and Zincon-Si-MNPs (B); HRTEM images of MNPs (C) and Zincon-Si-MNPs (D).

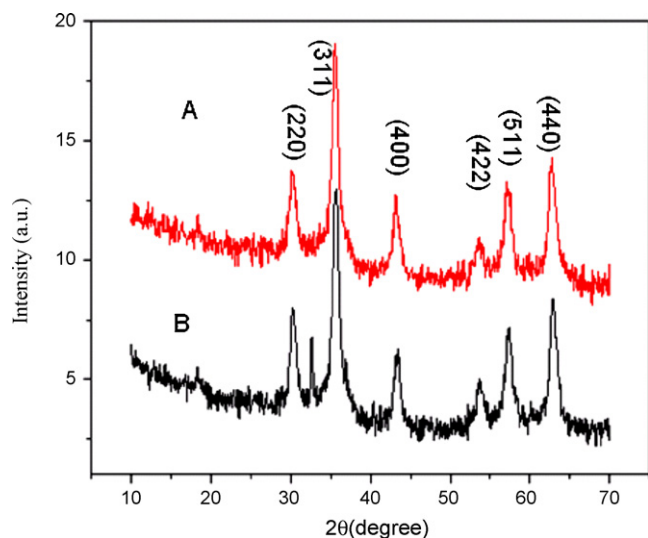


Fig. 5. XRD patterns of MNPs (A) and Zincon-Si-MNPs (B).

from 4 to 6. After pH was higher than 6, the recovery reached 90% and then remained constant. In other words, Pb was quantitatively adsorbed on Zincon-Si-MNPs at pH range 6–9. Lead is retained on Zincon-Si-MNPs mainly because it could form stable chelate with N-containing groups existing in zircon. For the purpose of reducing interference from the matrix at the practical pH value of environment samples, pH of 6.5 was selected in the following experiments.

### 3.2.2. Effect of eluent

As can be seen from Fig. 6 that Pb was almost not retained on Zincon-Si-MNPs when pH was less than 3, which means that

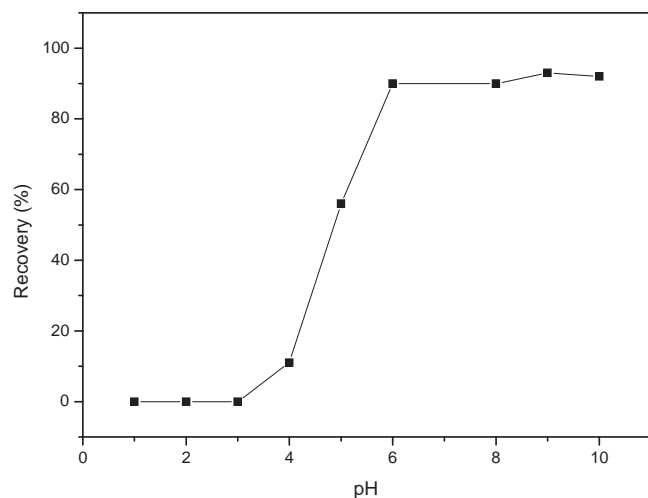


Fig. 6. Effect of pH on the recovery of Pb on Zincon-Si-MNPs. Pb: 50 ng mL<sup>-1</sup>.

Table 2

Comparison of analytical performance with different adsorbents used in SPE-GFAAS method.

Absorbent used in SPE-GFAAS method	LOD/ng L <sup>-1</sup>	Capacity/mg g <sup>-1</sup>	Enrichment factor	Analytical time/min	Reference
Zincon-Si-MNPs	10	21.5	200	2	This work
MCI GEL CHP 20Y	1.3	–	300	31	[10]
l-Alanine immobilized on carbon nanotubes	10	–	40	3	[11]
Pb(II)-imprinted polymer in nano-TiO <sub>2</sub>	47,000	22.7	–	240	[36]
Nano-TiO <sub>2</sub> immobilized on silica gel	9.5	3.16	50	25.5	[37]
MnO <sub>2</sub> coated carbon nanotubes	4.4	6.7	100	61.5	[38]

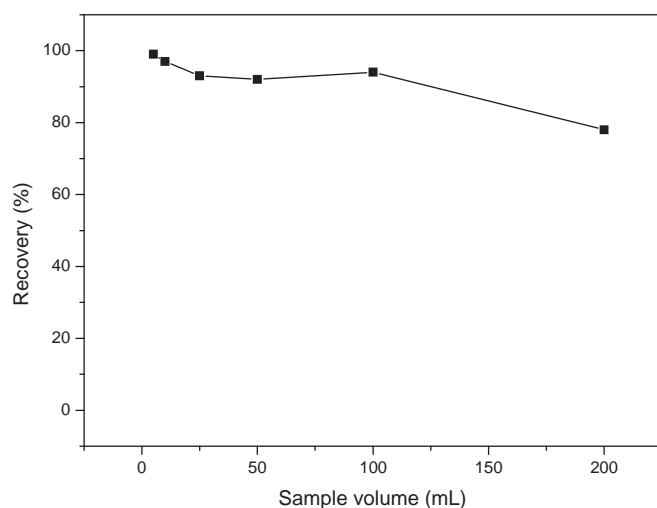


Fig. 7. Effect of sample volume on the recovery of Pb on Zincon-Si-MNPs. Pb: 50 ng mL<sup>-1</sup>; pH = 6.5; eluent: 0.5 mL, 1 mol L<sup>-1</sup> HCl; adsorption and desorption time: 2 min.

Pb reserved on adsorbent could be desorbed by acid. Therefore, the influence of concentration and volume of HCl on the recovery of Pb was explored. The concentration of HCl was evaluated in the range of 0.1–2 mol L<sup>-1</sup> and the result indicated that Pb can be quantitatively eluted in the whole HCl concentration range studied. Thus, the HCl concentration of 1 mol L<sup>-1</sup> was chosen in this work. Meanwhile, the result about the HCl solution volume on Pb recovery indicated that Pb can be quantitatively stripped from Zincon-Si-MNPs in the volume range of 0.5–5 mL. In order to achieve high enrichment factor, a small volume of 0.5 mL, 1 mol L<sup>-1</sup> HCl was used to elute Pb.

### 3.2.3. Effect of ultrasonic time

In order to obtain an appropriate experimental time, the effect of ultrasonic time on the adsorption and desorption was examined, respectively. The ultrasonic time was varied in the range of 1–10 min for both adsorption and desorption. It was observed that 2 min was sufficient for achieving satisfactory adsorption and desorption, which indicated that it is a very fast extraction process. The shortened analysis time is a significant advantage of the Zincon-Si-MNPs over other adsorbents such as silica-gel and common nanometer materials because of their high surface area-to-volume ratio and fast magnetic separation. Hence 2 min was selected as adsorption and desorption time.

### 3.2.4. Effect of sample volume

In order to examine the possibility of enriching low concentrations of analyte from large volumes, the effect of sample volume on the recovery of Pb was also studied. As shown in Fig. 7, quantitative recoveries (>90%) were obtained when sample volumes were less than 100 mL. So, a theoretical enrichment factor of 200 was achieved by this method.

**Table 3**  
Determination of Pb in environmental water samples (mean  $\pm$  S.D.,  $n = 3$ ).

Sample	Added/ng mL <sup>-1</sup>	Found/ng mL <sup>-1</sup>	Recovery/%
Tap water	0	0.680 $\pm$ 0.002	–
	0.5	1.230 $\pm$ 0.005	104
	1	1.690 $\pm$ 0.010	101
Yibao mineral spring water	0	0.240 $\pm$ 0.020	–
	0.1	0.290 $\pm$ 0.003	85
	0.5	0.660 $\pm$ 0.002	89
Jingtian mineral spring water	0	0.130 $\pm$ 0.006	–
	0.1	0.210 $\pm$ 0.003	91
	0.5	0.530 $\pm$ 0.010	84
Wahaha purified drinking water	0	–	–
	0.5	0.520 $\pm$ 0.020	104
	1	0.950 $\pm$ 0.003	95

### 3.2.5. Influence of co-existing ions

In order to demonstrate the selectivity of the developed magnetic SPE protocol for the determination of Pb, the effect of alkali, alkaline earth and heavy metals, which are common elements in environmental waters, on the measurement of 5 ng mL<sup>-1</sup> Pb was examined. The results showed that 0.5 mg mL<sup>-1</sup> K<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup>, 0.25 mg mL<sup>-1</sup> Mg<sup>2+</sup>, 10  $\mu$ g mL<sup>-1</sup> Ba<sup>2+</sup> and Zn<sup>2+</sup>, 5  $\mu$ g mL<sup>-1</sup> Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup> and Cd<sup>2+</sup> and 2.5  $\mu$ g mL<sup>-1</sup> Cr<sup>3+</sup> and Mn<sup>2+</sup> had no interferences with the determination of the Pb. The above results indicated that the developed method is suitable for the analysis of Pb in natural and drinking waters.

### 3.2.6. Analytical performance

According to the definition of IUPAC, limit of detection (LOD) was determined from the three times of standard deviation ( $3\sigma$ ) of 10 consecutive runs of blank solution. The LOD of this method was 10 ng L<sup>-1</sup> with an enrichment factor of 200. The relative standard deviations (RSDs,  $n = 5$ ) were 8.3% at 5 ng mL<sup>-1</sup>, 7.8% at 0.5 ng mL<sup>-1</sup> and 9.2% at 0.05 ng mL<sup>-1</sup> for Pb under the optimized conditions. The adsorption capacity is an important factor corresponding to the performance of the adsorbent. The capability study was adapted from the method recommended by Maquieira et al. [35]. The static adsorption capacity of Zincon–Si–MNPs to Pb was 21.5 mg g<sup>-1</sup>. Regeneration is another important factor for evaluating the performance of the adsorption material. It was observed that Zincon–Si–MNPs can be re-used up to three times without loss of analytical performance.

In addition, a comparison of the analytical performance obtained by this method with those reported with different adsorbents used in SPE–GFAAS approaches for the analysis of lead is shown in Table 2. The method in this work displayed good sensitivity, high enrichment factor and large adsorption capacity just using very short analytical time, implying that Zincon–Si–MNPs is a very attractive adsorbent for Pb analysis.

### 3.2.7. Analysis application

The developed method was applied to the determination of Pb in two mineral spring waters, a purified drinking waters and a tap water, and the analytical results along with the recoveries by spiking Pb<sup>2+</sup> to the water samples are given in Table 3. As can be seen, the recoveries of 84–104% were achieved for the spiked samples. In order to validate the proposed procedure, the method was used for the determination of the concentration of Pb<sup>2+</sup> in certified reference material of GBW08607 environmental water. The determined value of 1.02  $\pm$  0.09 mg L<sup>-1</sup> was in good agreement with the certified value of 1.04  $\pm$  0.02 mg L<sup>-1</sup>.

## 4. Conclusion

A novel surface modified superparamagnetic nanoparticles, Zincon–Si–MNPs, was synthesized and used as a SPE adsorbent to separate and preconcentrate trace Pb prior to the determination by GFAAS. Compared with common SPE adsorbents, the new adsorbent shows good sensitivity, high enrichment factor and large adsorption capacity especially just using very short analytical time, indicating that this is a very effective and attractive magnetic SPE adsorbent. Furthermore, magnetic SPE procedure is very easy to operate and different metals can be selectively reserved on MNPs with proper surface modification.

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