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ARTICLE

Preparation of dithizone grafted poly(allyl chloride) core-shell-shell magnetic composite microspheres for solid-phase extraction of ultra-trace levels of Pb(II), Cu(II) and Cr(III) ions

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A novel adsorbent with high adsorption efficiency and adsorption capacity was synthesized and applied to capture of heavy metal ions by coupling with ICP-OES analysis. The adsorbent consists of a magnetite (Fe₃O₄) core, a shell composed of polymerized 3-(trimethoxysilyl) propyl methacrylate, and another poly(allyl chloride) shell composing plenty of repetitive units, on which the complexing agent of dithizone was grafted by reaction with side chains of polymer. Compared with traditional adsorbent, the core-shell-shell magnetic composite microspheres have advantages of quick magnetic separation, excellent mechanical strength and high adsorption capacity. The adsorbent was characterized by scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, vibrating sample magnetometer, X-ray photoelectron spectrum, nitrogen adsorption surface area (BET), and FT-IR. Effects of enrichment conditions including pH, amount of adsorbent and elution conditions, interference of other coexistent ions, and the kinetics characterization and adsorption capacity of the adsorbent were studied. Under the optimized conditions, the limits of detection of Pb(II), Cu(II) and Cr(III) ions were 0.87, 0.079 and 0.029 μg L⁻¹, respectively. The RSDs(c=10 μg L⁻¹, n=7) were 2.33 %, 5.20 % and 1.30 %, respectively. This adsorbent was successfully applied to the analysis of certified reference materials, viz. a multi-element stock standard solution [(GBW(E)082083] and tea-leaf [GBW(E)080001], and environmental and biological samples.

Introduction

In recent years, heavy metal elements discharged from plating plants, mining, metal finishing, welding and alloy manufacturing threaten the environment safety and public health.

5 According to the World Health Organization (WTO), heavy metal elements such as lead and mercury are considered toxic and extremely dangerous even at trace levels, since they couldn't be metabolized by the body and would accumulate in soft tissues [1]. Heavy metals can easily enter the food chain through a number of pathways and gradually accumulate in living organisms to cause heavy metal poisoning. Thus, more and more researchers focus on detecting trace amounts of heavy metals [2]. However, in the analysis of real samples, due to the presence of potential contaminants and the complexity of matrices, the sample pretreatment techniques are often employed for ultra-trace analytes.

Numerous sample preparation procedures have been developed for detection of trace heavy metals such as liquid-liquid extraction (LLE) [3, 4], cloud point extraction [5, 6], chemical precipitation [7, 8], ion exchange [9] and solid-phase extraction (SPE) [10, 11]. The magnetic solid-phase extraction (MSPE) is one of the most popular techniques, which has advantages of simple operation, quick and easy separation from matrix, higher enrichment factors, lower cost and reduced consumption of organic solvents as well [12].

One of the most important factors in development of magnetic solid-phase extraction method is magnetic adsorbent. In recent years, more and more attention has focused on the surface functionalized magnetic nanoparticles. Cui et al [13] developed a method for magnetic solid phase extraction of trace-levels of Hg(II) ions by using Fe₃O₄ nanoparticles (NPs) covered with a shell of silica and modified with the chelator N-(2-acetyl aminoethyl)-N'-(3-triethoxysilylpropyl)thiourea. Zhai et al [14] established a simple and rapid MSPE method using diphenylcarbazide-doped silica-coated magnetic nanoparticles, for selective sampling of Hg(II) in environmental and biological samples. Cheng et al [15] prepared mercapto-containing dithizone (H₂Dz) modified silica-coated magnetic Fe₃O₄ nanoparticles (SCMNPs), and applied them to develop MSPE method for the detection of trace Cr(III), Cu(II), Pb(II) and Zn(II) in environmental and biological samples. Mahrouz Alvand et al [16] reported the Graphene-based magnetic nanoparticles (G-Fe₃O₄) as an effective adsorbent to detect trace quantities of cadmium from water and vegetable samples. Liu et al [17] had reported a reusable adsorbent magnetic cellulose-chitosan hydrogels with high adsorption capacity by ionic liquids. Some researcher also prepared magnetic microspheres coated with polymers with core-shell nanostructures, because the polymer shell prevents the core part from particle-particle aggregation and improves the dispersion stability of the core-shell nanostructures in suspension medium [18]. Badruddoza et al [19] reported the

magnetic nanoparticles with carboxymethyl- β -cyclodextrin polymer grafted, which had the complexing abilities of the multiple hydroxyl and carboxyl groups in polymer backbone with metal ions. Ge et al.^[20] prepared copolymers of acrylic acid (AA) and crotonic acid (CA) modified magnetic Fe₃O₄ nanoparticles for removing heavy metal ions (Cd²⁺, Zn²⁺, Pb²⁺ and Cu²⁺) from aqueous solution.

Dithizone is a widely used chelating agent with metal-binding functional groups^[21]. According to the hard and soft acids and bases (HSAB) theory introduced by Pearson, oxygen, nitrogen, and sulfur atoms are regarded as metal-binding atoms with strong affinity for heavy metal ions like lead, cadmium, mercury, etc.^[22]. So, dithizone can be expected as an efficient chelating agent for heavy metal ions because of its chemical composition. Herein, in our work, a novel magnetic adsorbent, dithizone grafted Fe₃O₄@MPS@poly(allyl chloride) microspheres with core-shell-shell structure was prepared and a corresponding MSPE method was developed for simultaneous detection of trace amounts of Pb(II), Cu(II) and Cr(III) ions in environmental and biological samples by ICP-OES. The adsorbent was coated with non-poisonous organosilanes agent to form a core-shell structure and modified another polymer layer via distillation-precipitation. Functionalized surface covered by abundant allyl chloride groups originated from repetitive structure unit on the side chains of polymer shell was formed because of distillation-precipitation. Compared with polymer prepared by terminal group modification, abundant allyl chloride groups coming from repetitive units on the side chains of polymer provide more active sites for modification of dithizone through substitution reaction.

Experimental

Apparatus

The simultaneous detection of Pb(II), Cu(II) and Cr(III) ions was performed on an Radial ICP-OES equipment (Agilent 725, USA) and the operating conditions are given in Table 1. The structure and surface morphology of microspheres were studied with scanning electron microscope (SEM, JSM-60LV, JEOL, Japan) and transmission electron microscope (TEM, JEM-2100, JEOL, Japan). The crystalline structure of microspheres was characterized by D/MAX 2550 VB/PC advance X-ray powder diffraction (XRD, RIGAKU, Japan) with a Cu K α source. The 2 θ angles probed were from 5° to 80° at a rate of 5° min⁻¹. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 40 °C to 800 °C (Pyris Diamond, PerkinElmer, USA). The dithizone grafted poly(allyl chloride) magnetic microspheres were characterized by the FTIR spectra (Nicolet 6700 FTIR, Thermo, USA) using the KBr pellet method. The saturation magnetization curve was

Table 1. Operation parameters of radial ICP-OES for this experiment.

RF generator power (W)	1200
Frequency of RF generator (MHz)	27.12
Coolant gas flow rate (L min ⁻¹)	15
Auxiliary gas (L min ⁻¹)	1.5
Plasma gas (L min ⁻¹)	0.75
Observation height (mm)	8
Integration times (s)	5
Analytical wavelength (nm)	Cr 267.7, Cu327.3, Pb 220.3

recorded on a Physical Property Measurement System 9T (Quantum Design, San Diego, USA) at room temperature. The X-ray photoelectron spectra were obtained using an ESCALAB 250Xi X-ray photoelectron spectrometer (XPS). The specific surface area was measured by N₂ adsorption surface areas (BET) on a Micromeritics Instrument Corporation TriStar II 3020 (USA).

Reagents and Materials

Dithizone, ethanol, ferric trichloride hexahydrate, anhydrous sodium acetate, copper chloride dihydrate, ethylene glycol ammonium hydroxide were analytical reagent grade and gained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 3-(trimethoxysilyl) propyl methacrylate (MPS, 98%), allyl chloride and ethylene glycol dimethacrylate (EGDMA, 98%) were purchased from Sigma-Aldrich (USA). 2,2'-azobis(2-methylpropionitrile) (ABIN) was obtained from Acros Organics (USA). A stock solution of copper ion was prepared by dissolving an appropriate amount of copper chloride dihydrate in double distilled water. A stock solution of chromium and lead ions was prepared by dissolving appropriate amount of corresponding nitrate salts in double-distilled water. Double deionized water (18 M Ω cm) was used throughout the experiments. The certified reference material multi-element stock standard solution (GBW(E)082083) was purchased from Shanghai Institute of Measurement and Testing Technology (SIMT). The certified reference material of tea-leaf (GBW(E)080001) was purchased from National Standard Materials Research Center, China.

Preparation of Fe₃O₄ magnetic particles.

The Fe₃O₄ magnetic nanoparticles were prepared by conventional method^[23]. Briefly, 2.7 g ferric trichloride hexahydrate was dissolved in ethylene glycol (100 mL) to form a clear orange yellow colour solution and followed by the addition of anhydrous sodium acetate (7.2 g). The mixture was sonicated and stirred vigorously in a round bottle to form homogeneous solution. Then, the solution was sealed in a PTFE-lined autoclave and reacted at 200 °C for 8 h. The resulting magnetic nanoparticles were separated by external magnetic force and then rinsed with water and ethanol for 3 times each, dried at 50 °C in a vacuum overnight.

Preparation of vinyl-functionalized Fe₃O₄@MPS microspheres

The core-shell vinyl-functionalized Fe₃O₄@MPS magnetic microspheres were synthesized according to the previous literature^[24] using MPS as the silane agent. Typically, 200 mg magnetic nanoparticles were redispersed in a medium containing 10 mL of deionized water, 40 mL of ethanol, and 1.5 mL of aqueous ammonia (25 wt %). Next, 0.3 mL MPS silane coupling agent was added to a three neck flask. After the suspension was mechanically stirred for 24 h at 60 °C, Fe₃O₄@MPS core-shell microspheres were isolated and washed several times with water and ethanol.

Preparation of poly-allyl chloride functionalized Fe₃O₄@MPS @ poly(allyl chloride) microspheres via distillation-precipitation

The core-shell-shell structured Fe₃O₄@MPS@poly(allyl chloride) magnetic composite microspheres were synthesized via distillation precipitation polymerization. Firstly, 50 mg Fe₃O₄@MPS core-shell microspheres were dispersed into 40 mL acetonitrile and sonicated for 10 min. Then, 200 μ L of allyl

chloride, 300 μL of EGDMA and 10 mg ABIN were successively added into the dispersion as monomer, cross-linking agent and initiator respectively. The mixture was heated by a boiling oil bath at 90 $^{\circ}\text{C}$, and the polymerization was accomplished under reflux condition for 1 h. The resulting $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ composite microspheres were harvested and washed through magnetic separation.

Preparation of dithizone grafted poly(allyl chloride) core-shell-shell magnetic microspheres

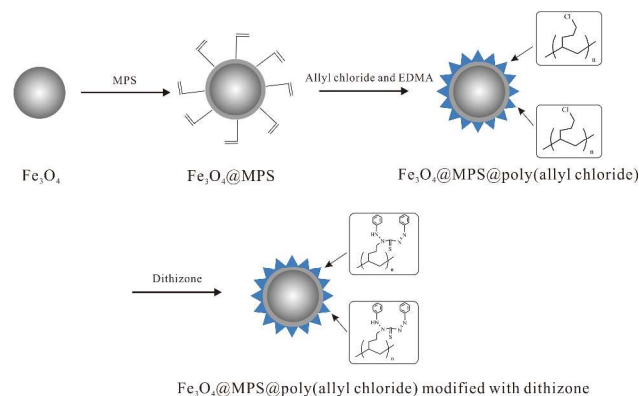
200 mg $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ core-shell-shell microspheres were dispersed in a medium containing 50 mL of trichloromethane and 50 mL of triethylamine solution by ultrasonication. Then, 200 mg dithizone was added to the dispersion solution. The reaction was mechanically stirred at 60 $^{\circ}\text{C}$ for 24 h. The product was washed by ethanol and water and dried at 50 $^{\circ}\text{C}$ in vacuum overnight.

Magnetic solid phase extraction procedure

10 mg of magnetic microspheres were added to 50 mL of sample solution containing the analytes and the pH of the solution was adjusted to 6 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions. The mixed solution was then shaken at room temperature for 10 min. Then, the magnetic adsorbent with analytes adsorbed was separated from the mixture using a permanent magnet. The analytes adsorbed on the magnetic adsorbent was eluted by 1.5 mL of 1.0 mol L^{-1} HCl solution and shaken for 10 min. Finally, the magnet was used again to separate the adsorbent, and the eluate was transferred into a test tube for detection by ICP-OES.

Real samples and sample preparation

In order to evaluate the developed method, the method was applied to detection of Pb(II), Cu(II) and Cr(III) ions in food and water samples. About 0.3 g of pork liver powder and 0.3 g of tea leaf (GBW(E)080001) were digested with 6 mL of concentrated HNO_3 for 2 h at 200 $^{\circ}\text{C}$. The resulted solution was transferred into 10 mL volumetric flask. Then, the solution was diluted to 10 mL before adjusting the pH to 6.0. The blank solution was prepared by adding the same amount of HNO_3 , followed by the digestion program. The water sample was adjusted to pH of 6.0 according to optimized experimental conditions before analysis. The beaker and volumetric flask were cleaned with detergent, water, diluted nitric acid and water in sequence.



Scheme 1. Synthetic procedure of dithizone grafted poly(allyl chloride) core-shell-shell magnetic microspheres.

Results and discussion

Preparation and Characterization of core-shell-shell magnetic microspheres

The preparation protocol of dithizone grafted $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ microspheres with a core-shell-shell structure is illustrated in Scheme 1. In this protocol, firstly, Fe_3O_4 was synthesized using solvothermal method and then 3-(trimethoxysilyl) propyl methacrylate was directly modified to introduce active vinyl groups and form core-shell structure. Then, another shell of poly(allyl chloride) was synthesized on the surface of magnetic microspheres via distillation-precipitation polymerization. Finally, the dithizone was grafted to the surface of core-shell-shell microspheres to get functionalized hybrid $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ magnetic microspheres through the substitution reaction with allyl chloride.

The SEM image shows that the dithizone grafted core-shell-shell magnetic microspheres have uniform size with average diameter of about 200 nm and well dispersity (Fig. 1A). The TEM image shows that the Fe_3O_4 particles have an average diameter of about 150 nm (Fig. 1B). After modification with MPS and the distillation-precipitation polymerization, the diameter increased to approximately 200 nm in diameter, corresponding to a 25 nm thick layer on the surface assigned to poly(allyl chloride). The core-shell-shell structure was clearly shown in the TEM image.

FT-IR spectra of $\text{Fe}_3\text{O}_4@\text{MPS}$, $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ and dithizone grafted $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ are shown in Fig. 2(A). The characteristic peak at 1046 cm^{-1} is assigned to the strong stretching vibration of Si-O-Si (Fig. 2(A) a.). The distinct adsorption peak at 1628 cm^{-1} is assigned to the vinyl group of MPS (Fig. 2(A) a.). After distillation-precipitation polymerization of allyl chloride, the strong adsorption peaks at 1727 cm^{-1} is attributed to stretching vibration of saturated aliphatic esters C=O (Fig. 2(A) b.). The typical peaks at 1258 cm^{-1} and 1159 cm^{-1} are attributed to the spectra bands of C-C(=O)-O (Fig. 2(A) b.). Meanwhile, the peak at 960 cm^{-1} of C-Cl stretching vibration appeared (Fig. 2(A) b.). After the poly(allyl chloride) shell reacted with dithizone, 1116 cm^{-1} and 806 cm^{-1} are attributed to the stretching vibration of C=S and the C-H bond of aromatic ring (Fig. 2(A) c.), which further confirmed that the dithizone was grafted onto the surface of magnetic microsphere.

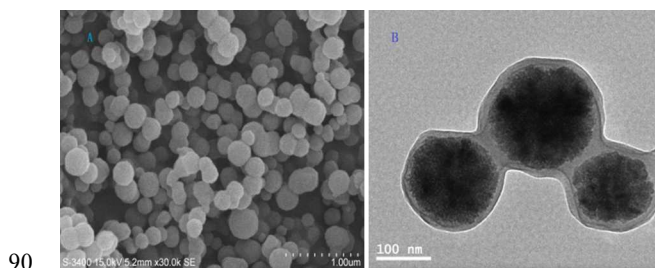


Figure 1. SEM (A, left) and TEM (B, right) of dithizone grafted $\text{Fe}_3\text{O}_4@\text{MPS@poly}(\text{allyl chloride})$ microspheres

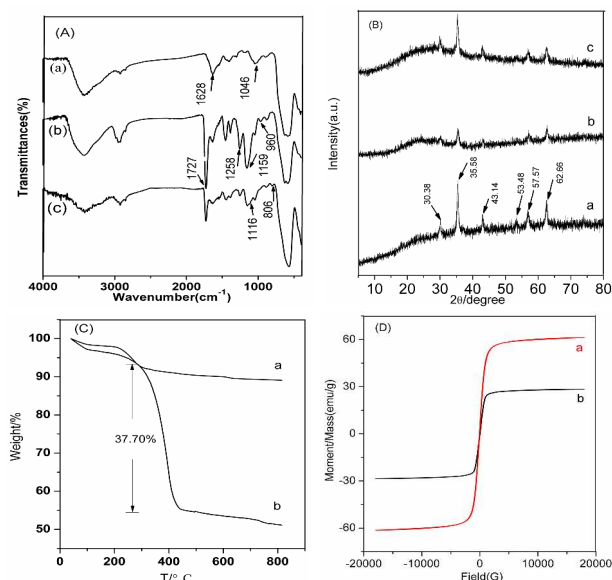


Figure 2. (A) The FT-IR spectra of Fe_3O_4 @MPS(a), Fe_3O_4 @MPS@poly(allyl chloride)(b) and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride)(c), (B) XRD patterns of Fe_3O_4 (a), Fe_3O_4 @MPS(b), and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride)(c), (C) TGA curves of Fe_3O_4 (a) and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride)(b), (D) The magnetic hysteresis loop of Fe_3O_4 (a) and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride)(b)

The crystalline structure of the synthesized Fe_3O_4 , Fe_3O_4 @MPS and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride) were analyzed by powder X-ray diffraction (XRD) (Fig. 2(B)). From the XRD spectra, in the 2θ range of 20 – 80° , the diffraction peaks of prepared Fe_3O_4 nanoparticles are consistent with the standard XRD spectrum of magnetic Fe_3O_4 . The XRD spectra of Fe_3O_4 @MPS and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride) also have the six characteristic peaks which are ascribed to crystal plane of (220), (311), (400), (422), (511) and (440), respectively. The XRD patterns also show that MPS and dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride) did not change the Fe_3O_4 phase.

The successful multi-step modification of Fe_3O_4 core by MPS, poly(allyl chloride) and dithizone was confirmed by TGA analysis too. As shown in Fig. 2(C), two weight loss peaks were observed on the TGA between dithizone grafted poly(allyl chloride) magnetic microspheres (curve b) and Fe_3O_4 (curve a). A very sharp weight loss occurred from 300°C to 410°C , which was from the MPS and dithizone grafted poly(allyl chloride) coating on the surface of Fe_3O_4 core. This indicated that approximately 37.7 wt % of as-prepared microspheres are MPS and dithizone grafted poly(allyl chloride) layers.

The magnetic properties of the two kinds of magnetic microspheres were studied by using a vibrating sample magnetometer at the room temperature (Fig. 2(D)). The magnetic hysteresis loop curves show the two kinds of materials have no obvious remanence or coercivity at the room temperature, suggesting that they are both supermagnetic. The saturation magnetization value of pure Fe_3O_4 core at the room temperature was 61.31 emu g^{-1} (Fig. 2(D) a). The saturation magnetization of dithizone

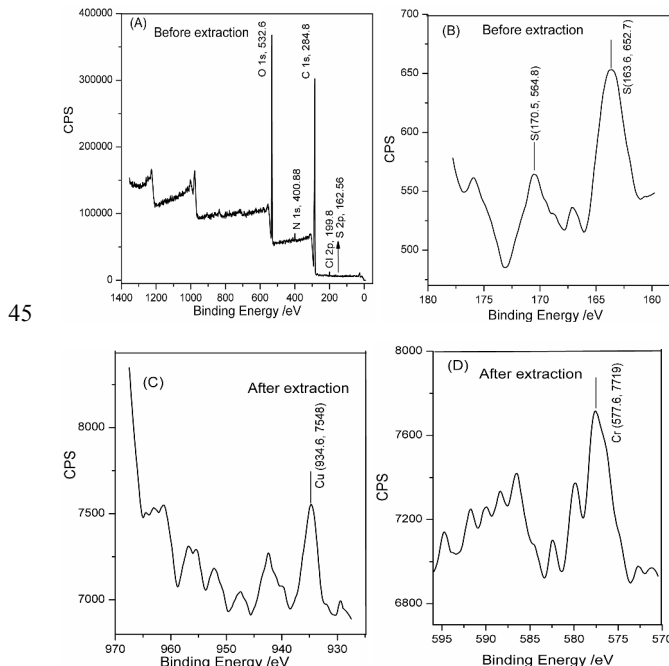


Figure 3. (A) The XPS spectra of dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride) before extraction heavy metal ions, (B) The XPS of S_{2p} before extraction, (C) The XPS of Cu_{2p} after extraction, (D) The XPS of Cr_{2p} after extraction.

grafted Fe_3O_4 @MPS@poly(allyl chloride) was reduced to 28.63 emu g^{-1} (Fig. 2(D) b), but it retained a strongly magnetic property at room temperature and allowed for effective magnetic separation. It implied that the core-shell magnetic composite microspheres can be simply and quickly separation by external magnetic field.

XPS spectra have been widely used to identify the existence of particular element on the surface of the material. The XPS spectra of the prepared materials before extraction of heavy metal ions are obtained shown in Fig. 3(A). The XPS spectra confirmed existence of C, O, N, Cl, S on the outside surface of the dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride) magnetic microspheres. Spectrum of Fe_3O_4 core inside the particle wasn't found. In the Fig. 3A, the peaks of C_{1s} at around 284.6 eV , O_{1s} at around 532.6 eV , N_{1s} at around 400.88 eV , and Cl_{2s} at around 199.8 eV were observed which demonstrated that the magnetic Fe_3O_4 core was coated by a thick polymer layer. The Cl_{2s} binding energy at 199.8 eV is associated with residual poly allyl chloride. As shown in Fig. 3(B), two peaks appeared at 163.6 eV and 170.5 eV are attributed to sulfur atoms of dithizone. This indicated that dithizone was grafted on the surface of magnetic microsphere. After extraction with 10 mL of 1.0 mg L^{-1} Cu(II) and Cr(III) ions, the peaks at about 934.6 eV and 577.6 eV are shown in Fig. 3(C and D), which are in agreement with Cu(II) and Cr(III) ions standard data^[25]. So, the XPS characterization revealed that dithizone was grafted on the surface of magnetic microsphere and the heavy metal ions being adsorbed on the surface of magnetic microsphere.

The content of sulfur (400 mg kg^{-1}) in the dithizone grafted Fe_3O_4 @MPS@poly(allyl chloride) was determined by ICP-OES, which indicated that dithizone ($0.32\text{ wt } \%$) was grafted on the surface of microsphere. The specific surface area of the Fe_3O_4

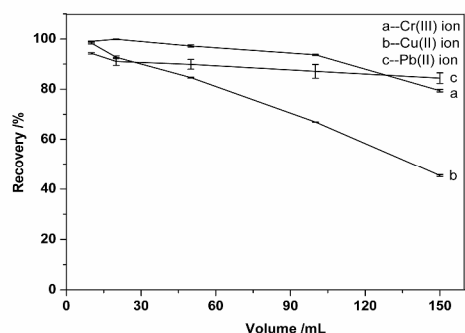


Figure 4. Sample volume effect on extraction recovery of heavy metal ions.

core is $13.26 \text{ m}^2 \text{ g}^{-1}$. After functionalization by polymer shell, the specific surface area of the dithizone grafted $\text{Fe}_3\text{O}_4@\text{MPS}@\text{poly}(\text{allyl chloride})$ is $35.48 \text{ m}^2 \text{ g}^{-1}$.

Optimization of parameters

In order to develop the MSPE method based on dithizone grafted $\text{Fe}_3\text{O}_4@\text{MPS}@\text{poly}(\text{allyl chloride})$, the extraction conditions including pH, amount of adsorbent, adsorption time, sample volume, the elution condition and interference from co-existing ions were studied to achieve maximal recovery. The following parameters were optimized: (a) sample pH value; (b) amount of adsorbent; (c) adsorption time; and (d) elution condition. Respective data and figures are given in the Electronic Supporting Information. The following experimental conditions were found to give the best results: (a) a sample pH value of $\text{pH}=6$; (b) 10 mg adsorbent; (c) 10 min adsorption time; (d) elution with 1.5 mL of 1.0 mol L^{-1} HCl for 10 min .

Effect of sample volume

In order to improve the enrichment factor, a large volume of sample is required. So the impact of sample volume on the recovery of target metal ions was studied in the range of $10 - 150 \text{ mL}$ with total sample amount of $10 \text{ }\mu\text{g}$. The experimental results are shown in Fig. 4. It was found that quantitative satisfied recoveries for all target analytes were obtained when the sample volume was less than 100 mL . But significant decrease was found for Cu(II) ion when the sample volume was larger than 50 mL . The recoveries were gradually decreased with increase of sample volume. So, the maximum sample volume of 50 mL for Cu(II) ion and 100 mL for Pb(II) and Cr(III) ions were chosen to reach the recovery higher than 90% . The real enrichment factors of 28.2 , 58.0 and 62.4 were achieved for Cu(II), Pb(II) and Cr(III) ions respectively by calculating the ratio between the analyte concentration in the

Table 2. Influence of co-existing ions

Co-existing ions	Tolerable concentration Ratio X/ Cr, Cu, Pb	R %		
		Cr	Cu	Pb
K^+	5000	99.8	102	96.2
Na^+	5000	95.9	96.6	84.2
Ca^{2+}	5000	89.7	100	91.4
Mg^{2+}	5000	101	91.9	85.2
Co^{2+}	100	106	93.7	81.8
NO_3^-	5000	99.4	101	95.9
Cl^-	5000	90.0	101	93.1

R: Recovery

eluting solution and the initial concentration of analyte in the sample, while the theoretical enrichment factors were 33.3 , 66.6 and 66.6 respectively.

Interference of co-existing ions

To demonstrate the suitability of the developed procedure, the interference of potentially interfering ions such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Co^{2+} , NO_3^- , Cl^- , which widely exist in common environment, was investigated under the above optimized conditions. The tolerance degrees for some alkaline, alkaline earth and transition metal ions are presented in Table 2. The experimental results showed that the recoveries of the target metal ions were remained above 81% in the presence of high concentration potentially interfering ions. It indicated that the method developed was suitable for analysis of Pb(II), Cu(II) and Cr(III) ions in real sample without masking reagents.

Analytical performance and analytical applications

Under the optimized experimental conditions, calibration curves were sketched for the detection of lead, copper and chromium ions according to the general procedure. The limit of detection is defined as $C_{\text{LOD}}=3S_b/m$, where S_b is the standard deviation of 11 replicate blank signals and m is the slope of the calibration curve. Under the linear range of $0 - 100 \text{ }\mu\text{g L}^{-1}$ for lead, $0 - 100 \text{ }\mu\text{g L}^{-1}$ for copper and $1 - 100 \text{ }\mu\text{g L}^{-1}$ for chromium ions, the regression equations were $A=5.027C (\text{ }\mu\text{g L}^{-1}) + 28.83$, with R^2 of 0.999 for lead, $A=119.6C (\text{ }\mu\text{g L}^{-1}) + 149.3$, with a correlation coefficient (R^2) of 0.999 for copper and $A=87.66C (\text{ }\mu\text{g L}^{-1}) + 5304$, with a correlation coefficient (R^2) of 0.997 for chromium ions, respectively. With the 50 mL of sample volume, the limits of detection of the developed method were 0.87 , 0.079 and $0.029 \text{ }\mu\text{g L}^{-1}$ for Pb(II), Cu(II) and Cr(III) ions, respectively. The RSDs ($c=10 \text{ }\mu\text{g L}^{-1}$, $n=7$) were 2.33% , 5.20% and 1.30% , respectively. Comparing with other solid-phase extraction reported in the literature, the method had a good sensitivity, low detection limit and high adsorption capacity (Table S2, ESI †).

To validate the accuracy of the developed method, two certified reference materials multi-element stock standard solution GBW(E)082083 and tea-leaf GBW(E)080001 were analyzed, and the results were listed in Table 3 and 4. From the results, the determined values were well agreed with the certified values with satisfactory recoveries. Therefore, the developed method can be used as a reliable solid-phase method for extraction and detection of Pb(II), Cu(II) and Cr(III) ions in

Table 3. Analytical results for certified reference material multi-element stock standard solution GBW(E)082083

Element	Certified value (mg L^{-1})	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
Cr	0.20 ± 0.002	0	0.199 ± 0.001	82.5
		0.200	0.388 ± 0.024	83.3
Cu	0.20 ± 0.002	0	0.165 ± 0.001	98.0
		0.200	0.332 ± 0.027	91.5
Pb	0.20 ± 0.002	0	0.196 ± 0.002	99.5
		0.200	0.379 ± 0.021	94.9

Table 4. Analytical results for certified reference material tea-leaf GBW(E)080001

Element	Certified value (mg kg ⁻¹)	Added (mg L ⁻¹)	Found (mg kg ⁻¹)	Recovery (%)
Cr	2	0	1.92 ± 0.32	96.0
		0.05	19.5 ± 0.42	102
Cu	8.96 ± 0.59	0	8.85 ± 0.47	98.7
		0.05	24.8 ± 0.46	95.7
Pb	1.00 ± 0.05	0	1.10 ± 0.36	110
		0.05	17.8 ± 2.9	101

real samples.

In order to demonstrate the performance of the method, the laboratory tap water and pork liver powder were also analyzed as real sample by magnetic solid-phase extraction. The analytical results along with the recoveries for the spiked samples were given in Table 5 and 6. For the tap water and the pork liver powder, the determined values of three target metal ions are with the recoveries of 83.2-101.4 %. The results show satisfactory recoveries for trace analysis.

The reproducibility and stability of the dithizone grafted magnetic microspheres were investigated under the optimum conditions. Ten microgram of magnetic microspheres were applied to adsorb 25 mL of sample solution containing 1.0 mg L⁻¹ analytes at pH of 6 for 10 min. Then the analytes were eluted by 1.5 mL of 1.0 mol L⁻¹ HCl for 10 min. After the 4 repeated cyclic adsorption and desorption, adsorption efficiency of the dithizone grafted magnetic microspheres still reached 95 % for Pb(II), Cu(II) and Cr(III) ions. For Cu(II), the adsorption efficiencies are 95.1%, 99.1%, 98.2% and 99.5% for four enrichments, respectively. The detailed experiment results are shown in Electronic Supplementary Information (Table S3, ESI †). The results further indicated that the dithizone grafted magnetic microspheres showed good stability and reproducibility.

Conclusions

In this work, the core-shell-shell Fe₃O₄@MPS@poly(allyl chloride) magnetic microspheres were prepared via distillation precipitation polymerization. The chelating agent dithizone which had strong affinity for heavy metal ions could be grafted on the side chains of polymer which had the repetitive units of allyl chloride through the substitution reaction. Magnetic

Table 5. Analytical results for laboratory tap water

Element	Determination value (mg L ⁻¹)	Added (mg L ⁻¹)	Found (mg L ⁻¹)	Recovery (%)
Cr	-	0	-	-
		0.020	0.018 ± 0.001	88.3
Cu	-	0	-	-
		0.020	0.017 ± 0.001	83.5
Pb	-	0	-	-
		0.020	0.018 ± 0.002	92.6

35 -: Not detected

Table 6. Analytical results for the pork liver powder

Element	Determination value (mg kg ⁻¹)	Added (mg L ⁻¹)	Found (mg kg ⁻¹)	Recovery (%)
Cr	-	-	-	-
		0.05	24.6 ± 0.86	98.8
Cu	10.5 ± 0.33	-	10.5 ± 0.33	-
		0.05	31.4 ± 0.13	101
Pb	-	-	-	-
		0.05	20.8 ± 4.8	83.2

separation made it easy to collect the adsorbent with an external magnet, thus avoiding the time consuming conventional column passing and filtration operations. The non-poisonous organosilanes agent coated on the magnetic microspheres enhanced the mechanical strength. On the other hand, a magnetic solid-phase extraction method was developed for simultaneous detection of trace amounts of Pb(II), Cu(II) and Cr(III) ions in environmental and biological samples by coupling with ICP-OES. Comparing with other solid-phase extraction, the developed method had a good sensitivity, low detection limit and high adsorption capacity. This method was also successfully applied to the analysis of environmental water samples, tea-leaf, pork liver powder and certified reference materials.

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