

Polythiophene-coated Fe₃O₄ nanoparticles as a selective adsorbent for magnetic solid-phase extraction of silver(I), gold(III), copper(II) and palladium(II)

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Received: 6 August 2013 / Accepted: 6 December 2013 / Published online: 19 December 2013
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Abstract We have developed a fast method for sensitive extraction and determination of the metal ions silver(I), gold(III), copper(II) and palladium(II). Fe₃O₄ magnetic nanoparticles were modified with polythiophene and used for extraction the metal ions without a chelating agent. Following extraction, the ions were determined by flow injection inductively coupled plasma optical emission spectrometry. The influence of sample pH, type and volume of eluent, amount of adsorbent, sample volume and time of adsorption and desorption were optimized. Under the optimum conditions, the calibration plots are linear in the 0.75 to 100 µg L⁻¹ concentration range ($R^2 > 0.998$), limits of detection in the range from 0.2 to 2.0 µg L⁻¹, and enhancement factors in the range from 70 to 129. Precisions, expressed as relative standard deviations, are lower than 4.2 %. The applicability of the method was demonstrated by the successful analysis of tap water, mineral water, and river water.

Keywords Fe₃O₄ magnetic nanoparticles · Polythiophene · Magnetic solid-phase extraction · Metal ions

Introduction

Precious metals are widely used in industry, agriculture and medicine, because of their specific physical and chemical properties. Precious metals are found in the process and wastewater streams of various industries including mining,

ore and metal processing, semiconductor and electronic manufacturing and e-Waste recycling [1,2]. The increasing use of silver compounds and silver containing products in industry and medicine has resulted in an increase of environmental silver content [3,4]. On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, vitamins E and B₁₂, has focused attention on its potential toxicity [5,6]. Palladium and its compounds find wide application in industry as a catalytic agent in different manufacture processes. Currently, significant amounts of palladium supported catalyst are disposed yearly from automobile and chemical industries as a hazardous solid waste [7–9]. World Health Organization had evaluated the risks to human health and the environment posed by exposures to Pd [10]. Health concern is the sensitization risk of Pd as very low doses are sufficient to cause allergic reactions in susceptible individuals [11]. Gold, one of the precious metals, has been widely used in many fields of modern society such as medicine, catalysis and electronics. During these application processes, gold species are inevitably leached into solutions, and as a result, a considerable quantity of gold-containing wastewater is produced, which create negative impacts on the environment. For example, Au³⁺ can interact with phospholipid bilayers to perturb the molecular structure of cells, and thus affect the permeability and functions of ion channels, receptors and enzymes immersed in the membrane lipid moiety [12,13]. Copper and its compounds are widely used in many fields of modern society, such as power transmission, plumbing and refining. During its application, a large quantity of Cu(II) contaminated wastewater is inevitably produced [14]. The uptaking of Cu(II) contaminated drinking water can cause serious health problems, including hemolysis, liver and kidney damage, fever with influenza syndrome, etc. [15]. Trace amount of Cu(II) is toxic enough to destroy the living tissues of fish, which further results in the breakdown of aquatic food chain [16].

Electronic supplementary material The online version of this article (doi:10.1007/s00604-013-1144-y) contains supplementary material, which is available to authorized users.

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Various analytical techniques have been established to determine metal ions such as flame atomic absorption spectroscopy (FAAS) [17–19], electrothermal atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry (ICP-OES) [20–23], inductively coupled plasma mass spectrometry and ultraviolet–visible spectrometry. Direct evaluation of the trace metal content in the complex matrices is still limited because of the complexity of the matrices in environmental samples and the frequently low concentrations of metals (near or below limit of detections of these techniques). The overcoming of these limitations simply achieved carrying out an effective extraction and preconcentration procedure before instrumental analysis. Among these sample preparation methods, solid-phase extraction (SPE) is the most common technique for routine analysis of samples with complex matrices because of its simplicity, rapidity, ability to attain a high concentration factor, reusability of the adsorbent, low cost, and low consumption of organic solvents.

Recently, many research studies have been focused on the development of nano-sized adsorbents in SPE procedure. Compared with micrometer-sized particles, nanoparticles (NPs) offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high extraction capacity, rapid extraction dynamics and high extraction efficiencies [24]. However, the nanosorbent in packed SPE column exhibits a high backpressure and so long sample loading time and in the static batch mode, the nanosized SPE adsorbents often lead to a very low filtration rate. Recently, utility and performance of magnetic nanoparticles (MNPs) as SPE adsorbents for preconcentration of trace level of organic and inorganic analytes have been investigated [25]. In the magnetic solid-phase extraction (MSPE) mode, magnetic nanosorbent is dispersed in sample solution and phase separation can be conveniently conducted by applying an external magnetic field outside the sample container but do not retain magnetism after the field is removed [25]. It should be pointed out that, bare MNPs were observed to aggregate easily to form a large aggregation, which may alter their magnetic properties. Also these nanometer-sized sorbent are not target selective and not suitable for samples with complicated matrices because of their low capacity [26–33]. Hence, surface modification can not only improve their dispersibility but also provide an active surface to interact with certain molecules.

In our previous study polythiophene coated Fe_3O_4 NPs ($\text{Fe}_3\text{O}_4@\text{PTh}$ NPs) was synthesized and used for extraction and preconcentration of three plasticizers from different environmental water samples [34]. In the present study, $\text{Fe}_3\text{O}_4@\text{PTh}$ NPs was applied for selective adsorption and extraction of four metal ions including Ag(I), Au(III), Cu(II) and Pd(II) without need to any chelating agent. To the best of our knowledge, this is the first report in which $\text{Fe}_3\text{O}_4@\text{PTh}$ NPs have been utilized as a magnetic sorbent for selective extraction of these four metal ions from water samples.

Experimental

Chemicals and reagents

All reagents used were of analytical grade. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonia solution 25 %, potassium permanganate (KMnO_4), acetonitrile, thiourea, hydrochloric acid and nitric acid were all purchased from Merck (Darmstadt, Germany, <http://www.merck.com>). Synthetic grade thiophene was obtained from Merck. The stock standard solutions ($1,000 \text{ mg L}^{-1}$) of Ag(I), Au(III), Cu(II), Pd(II) and Y(III) were prepared by dissolving appropriate amounts of analytical grade AgNO_3 , HAuCl_4 , $\text{CuNO}_3 \cdot 3\text{H}_2\text{O}$, PdCl_2 and $\text{Y}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ salts from Merck in ultra-pure water, respectively. Mixed working standard solutions were prepared by diluting the stock solutions with ultra-pure water. Ultra-pure water was prepared by an Aqua Max-Ultra Youngling ultrapure water purification system (Dongan-gu, South Korea, <http://www.younglin.com>).

It is worthy to mention that the standard solution (10 mg L^{-1}) of Y(III) as internal standard was added to all eluates injected to ICP-OES, and peak area of each analyte was divided to Y(III) peak area at 377.433 nm.

Instrumentation

A radial view Varian Vista-Pro simultaneous inductively coupled plasma optical emission spectrometry (Springvale, Australia, <http://www.agilent.com>) equipped with a concentric nebulizer and Scott spray chamber utilizing a charge coupled device (CCD) as detector was applied for determination of target metal ions. Operational conditions and selected wavelength for target ions were optimized and summarized in Table S1 (Electronic Supplementary Material, ESM). A silicon tube (with internal volume of $250 \mu\text{L}$) was used as a loop and was connected to a six-port two-position injection valve from Tehran University (Tehran, Iran) for flow injection introduction of the final solution to ICP-OES. All of the pH measurements were performed with a WTW Inolab pH meter (Weilheim, Germany, <http://www.inolab.de/en>).

Preparation of polythiophene-coated Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{PTh}$ NPs)

The preparation of polythiophene-coated Fe_3O_4 nanoparticles was performed according to our previous published work [34].

Procedure for magnetic solid phase extraction (MSPE)

Extraction procedure of metal ions was performed by batch equilibrium technique. First, 100 mL of sample solution spiked with the proper amounts of the target metal ions was

placed in a beaker and its pH was adjusted to 4 (by addition of dilute HNO₃ or NaOH). Afterwards, 60 mg of nanosorbent was dispersed into the solution. After being mechanical stirring for 8 min, the adsorbent were isolated from the suspension with a Nd-Fe-B magnet (10×5×4 cm with 1.4 T magnetic field). Subsequently, 400 μL of eluent (1 M thiourea in 0.01 M HNO₃) was introduced to desorb the adsorbed analytes from the adsorbent surface by fierce vortex for 1 min. Finally, eluate was magnetically separated and 250 μL of this solution was introduced into the nebulizer of the ICP-OES using the six-way two-position injection valve.

Results and discussion

Optimization of MSPE conditions

To obtain the highest extraction efficiency, various extraction parameters including sample pH, type and volume of eluent, adsorbent amount and times of adsorption and desorption were optimized. All the experiments were performed in triplicates and their average was used as analytical signal.

Selection of the most effective eluent for the quantitative stripping of the retained target metal ions onto the adsorbent is of special interest. To this reason, various concentrations of thiosulfate, thiourea, HNO₃ and thiourea-HNO₃ mixed solutions were used as eluent to desorb the adsorbed analytes. By using the acidic eluent, the donor atoms (S) of the adsorbent are protonated and the complexes of metal ions and adsorbent become weak. On the other hand, the thiourea can make complexes with metal ions and stripes them from the adsorbent. The obtained results are presented in Fig. 1. From the results, it was found that 0.01 M HNO₃ solution is suitable for the elution of palladium, and 1 M thiourea is suitable for gold and silver desorption, while, copper can be eluted by both of thiourea (1 M) and HNO₃ (0.01 M). As can be seen from Fig. 1, simultaneous elution of the studied metal ions could be obtained with solution of 1 M thiourea in 0.01 M HNO₃ and so it was applied as optimum eluent in subsequent experiments.

Acidity of the sample solution plays a significant role in the extraction of target metal ions by affecting their adsorption due to both the chemistry of target metal ions in solution and the protonation of the adsorbent donor atoms. Therefore, extraction efficiency of the target metal ions on the adsorbent surface as a function of the pH of the sample solution was evaluated. The results (Fig. 2) demonstrated that the maximum adsorption efficiency was occurred at pH 2 for Au³⁺ and 3 for Pd²⁺. While, extraction efficiency of Cu²⁺ and Ag⁺ increased by increasing of pH from 2 to 4 and reached to its maximum at pH 4, followed by decrease in extraction efficiency. At higher pH values, decrease in the extraction efficiency may be explained by the formation and precipitation of

hydroxide species of target metal ions. In strong acidic solutions, decrease in the extraction efficiency was probably due to the surface protonation of the adsorbent (sulfur donor atoms) and occupation of active sites by protons rather than target metal ions. According to obtained results, pH=4 was selected in subsequent experiments to reach better extraction efficiency for all of the metal ions.

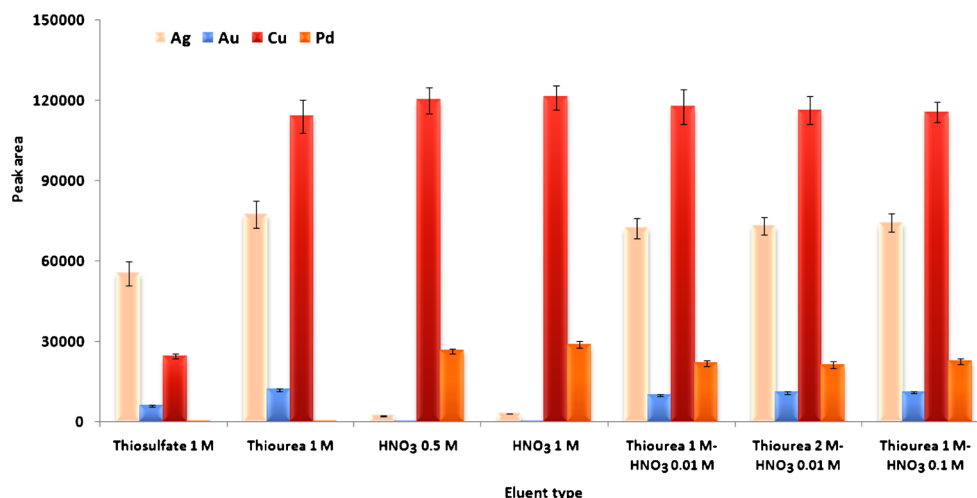
The obtained results from investigation of the type of the acid used for sample pH adjustment illustrated that extraction efficiency of Ag⁺, Au³⁺ and Pd²⁺ ions decrease when the sample solution pH was adjusted by using HCl as compared to HNO₃. This observation is due to the fact that Ag⁺ ions can form precipitate of AgCl, and Au³⁺ and Pd²⁺ ions can transform to anionic species with chloride anions (at higher concentrations of Cl⁻, pH<2). According to obtained results, pH adjustment was performed by using HNO₃ solution in subsequent experiments.

The investigation of adsorbent amount was performed at the range of 20 to 80 mg of the adsorbent and results are shown in Fig. 3(a). As can be seen, extraction efficiency was increased up to 60 mg of adsorbent for Cu²⁺, however, lower amounts of sorbent is sufficient for three other elements. By increasing the adsorbent amount, access sites of the adsorbent increases so extraction efficiency increases, too. However, the adsorption efficiency was decreased with a further increase of the adsorbent amount because of weak elution of the adsorbed analytes by a fixed volume of the eluent. Therefore, for further experiments, adsorbent amount of 60 mg was applied.

In order to increase the preconcentration factor as much as possible, large volume of sample solution is favorable. For this purpose, the effect of sample volume on extraction efficiency of target analytes was studied in the range of 40–200 mL and the obtained results are shown in Fig. S1 (Electronic Supplementary Material, ESM). As can be seen, no obvious influence of increasing sample volume on the extraction efficiency of the target analytes was observed until 100 mL and further increasing resulted in decrease in efficiency. It attributes to the more difficult transport of target analytes onto the adsorbent surface in larger volume of sample, because of lower amount of adsorbent in volume unit of the sample solution. Hence, volume of 100 mL was selected as optimum volume.

The extraction time was investigated to achieve the distribution equilibrium of analytes between the aqueous sample solution and the adsorbent. For this purpose, extraction times were studied between 2 and 12 min. According to the results that were shown in Fig. 3(b), the extraction of the target analytes slightly increased with the time up to 8 min and after that, it almost remained constant. Therefore, their distribution reached equilibrium after 8 min. However, after 5 min there was no significant increase in extraction efficiency but time of 8 min was chosen as the most appropriate extraction time. Short extraction time is one of the advantages of MSPE by a nanosorbent.

Fig. 1 Effect of eluent type on extraction efficiency. Extraction conditions: sample solution, 40 mL of $100 \mu\text{g L}^{-1}$ of Au^{3+} , Cu^{2+} and Pd^{2+} , and $30 \mu\text{g L}^{-1}$ of Ag^+ at pH=5; 20 mg of $\text{Fe}_3\text{O}_4@\text{PTh}$ NPs; 200 μL eluent; extraction time, 5 min; desorption time, 1 min



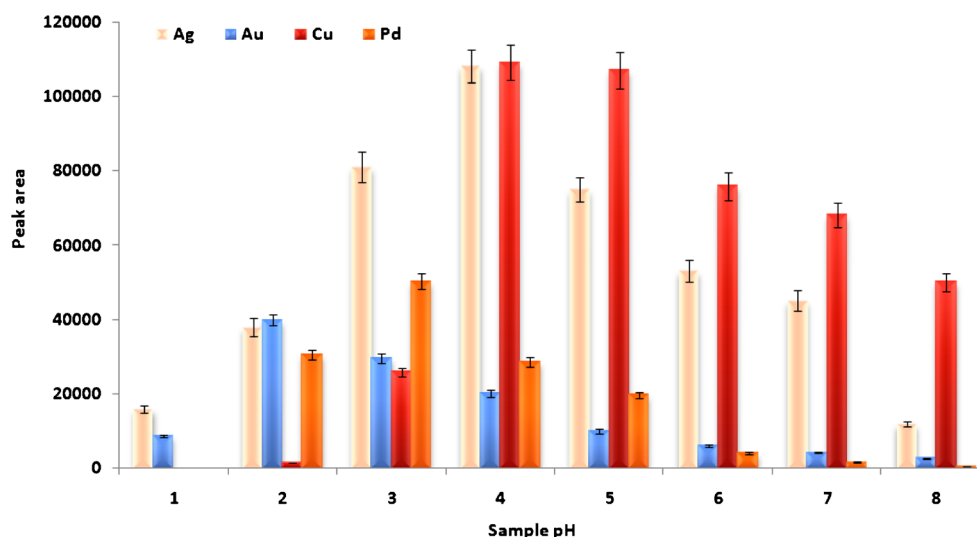
The optimum volume of the eluent to reach the better desorption efficiency and enrichment factor was also determined. As shown in Fig. S2 (ESM), the peak areas of the target metal ions increased by increasing the volume of the eluent from 100 to 400 μL , and then decreased with the further increase of the volume, because of dilution of the eluate. Lower eluent volumes were not studied in this work due to difficult swimming of the adsorbent into the eluent for complete desorption of the analytes. The minimum volume of the eluent required for a quantitative elution of the retained analytes was found 400 μL . Therefore, 400 μL of the eluent was selected in the following studies.

The effect of desorption time was also studied, and it was revealed that within 1 min, the target analytes could be quickly desorbed and more desorption times was not necessary.

Effect of potentially interfering elements

The interference effect of potentially interfering ions on extraction and determination of target analytes was examined

Fig. 2 Effect of sample pH on extraction efficiency. Extraction conditions: sample solution, 40 mL of $100 \mu\text{g L}^{-1}$ of Au^{3+} , Cu^{2+} and Pd^{2+} , and $30 \mu\text{g L}^{-1}$ of Ag^+ ; 20 mg of $\text{Fe}_3\text{O}_4@\text{PTh}$ NPs; 200 μL of 1 M thiourea in 0.01 M HNO_3 as eluent; extraction time, 5 min; desorption time, 1 min

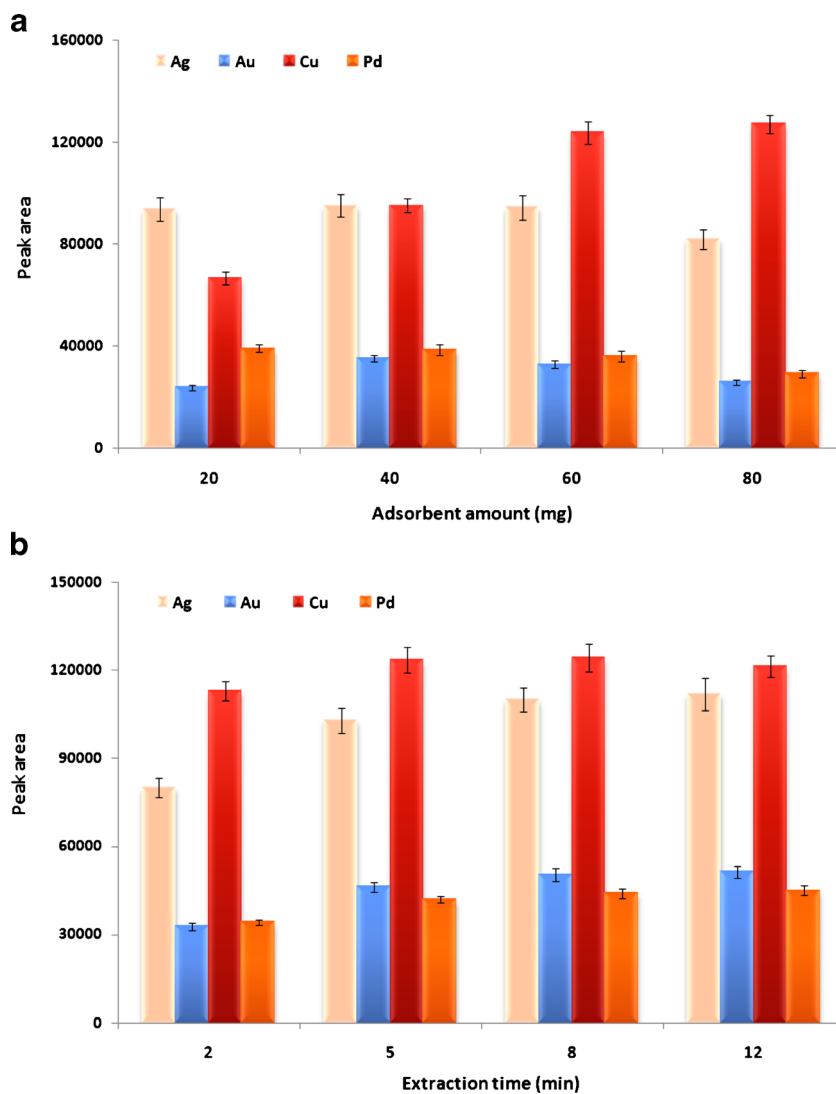


under the optimum conditions. Solutions containing $100 \mu\text{g L}^{-1}$ of target ions and different concentrations of the potentially interfering ions were prepared and treated according to the developed method in order to determine the selectivity of the adsorbent. The tolerance limits of the potentially interfering ions, defined as their highest amount which results in the recovery of the studied species in the 90–110 % interval, are given in Table 1. The results showed that the recoveries of the target metal ions were not affected by matrix interferences even in high concentrations. Thus, the adsorbent showed a good efficiency for extraction of Ag^+ , Au^{3+} , Cu^{2+} and Pd^{2+} ions, and a high selectivity toward the target metal ions was observed.

Selectivity of the sorbent and specific separation of studied metal ions

To investigate selectivity of the sorbent respected to the target metal ions extraction capability of some other metal ions was investigated by the sorbent. For this purpose, extraction

Fig. 3 a. Effect of adsorbent amount on extraction efficiency. Extraction conditions: sample solution, 40 mL of 100 $\mu\text{g L}^{-1}$ of Au³⁺, Cu²⁺ and Pd²⁺, and 30 $\mu\text{g L}^{-1}$ of Ag⁺ at pH=4; 200 μL of 1 M thiourea in 0.01 M HNO₃ as eluent; extraction time, 5 min; desorption time, 1 min.
b. Effect of extraction time on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100 $\mu\text{g L}^{-1}$ of Au³⁺, Cu²⁺ and Pd²⁺, and 30 $\mu\text{g L}^{-1}$ of Ag⁺ at pH=4; 60 mg of Fe₃O₄@PTh NPs; 200 μL of 1 M thiourea in 0.01 M HNO₃ as eluent; desorption time, 1 min



possibility of Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺, Cr³⁺ and Pb²⁺ ions were evaluated under optimum conditions. The obtained results demonstrated that the sorbent can't extract these metal ions. It is considered that the extraction of Ag⁺, Au³⁺, Cu²⁺ and Pd²⁺ ions by Fe₃O₄@PTh NPs occurs via complex formation between the sulfur atoms of polythiophene and metal ions according to hard/soft- acid/base theory. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson [35], metal ions will have a preference for complexing with ligands that have more or less electronegative donor atoms. Chelating agents with S groups are highly efficient for the selective sorption of precious metal ions. The sulfur group is known to form stable complexes with metal ions such as Ag⁺, Au³⁺, Cu²⁺ and Pd²⁺ due to the HSAB theory. These ions are known as a soft Lewis acid and S atom is softer donor atom than oxygen and nitrogen atoms. Thus, the studied metal ions show affinity especially to S atoms located on the sorbent. While Fe²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cr³⁺ and Pb²⁺ metal ions are

hard bases and don't have any tendency to the soft donor atom (S) of the sorbent.

However, this sorbent was introduced for selective extraction of trace amount of these four metal ions, but it can be used for their specific separation and recovery from some factory wastewaters. According to the results of the investigation of effects of sample pH and eluent type, by selecting the suitable pH and eluent, specific separation of these four metal ions can be obtained.

Specific separation of Cu²⁺ can be performed by adjusting the pH of the solution at 7 or higher and elution with HNO₃ solution (at this pH, only copper and silver can be adsorbed onto the sorbent while, by using the HNO₃ solution for elution, only copper can be specifically desorbed while silver cannot be eluted). For specific separation of palladium, pH should be adjusted at 2 and elution should be performed by using HNO₃ solution. At this pH, silver, gold and palladium can be adsorbed while only palladium can be desorbed by

Table 1 Tolerance limit of potentially interfering ions in extraction and determination of target metal ions

Potentially interfering ions	Ag ⁺ ^a		Au ³⁺ ^a		Cu ²⁺ ^a		Pd ²⁺ ^a	
	Ratio ([Ion]/[Ag ⁺])	RR% ^b	Ratio ([Ion]/[Au ³⁺])	RR%	Ratio ([Ion]/[Cu ²⁺])	RR%	Ratio ([Ion]/[Pd ²⁺])	RR%
Li ⁺	500	91	50	90	10000	98	10000	103
Na ⁺	2000	96	10000	95	10000	105	10000	92
K ⁺	4000	91	10000	92	10000	97	10000	93
Ca ⁺²	5000	96	5000	102	5000	91	5000	93
Mg ²⁺	10000	100	10000	93	10000	98	10000	91
Zn ²⁺	1000	96	1000	98	500	90	1000	102
Ni ²⁺	1000	99	1000	97	1000	104	1000	96
Co ²⁺	500	90	500	99	500	90	1000	90
Cr ³⁺	100	102	50	92	50	95	100	90
Pb ²⁺	100	94	1000	98	50	99	50	93
Hg ²⁺	80	90	30	93	30	96	30	91
Cl ⁻	350	94	50	92	30000	98	100	91
PO ₄ ⁻³	100	97	100	95	100	94	100	92
SO ₄ ⁻²	500	92	300	98	500	97	300	93

^a Concentrations of target metal ions are 100 µg L⁻¹

^b Relative recovery%

HNO₃ solution. Unfortunately, silver and gold cannot be separated specifically by this system and they can be separated from the other metal ions by adjusting the pH at 2 and elution with thiourea solution. At this case, adsorbed palladium cannot be desorbed while silver and gold can be desorbed and separated from the other ions.

Reusability studies

To evaluate the possibility of reusing and regenerating the sorbent, reusability tests were performed by several consecutive adsorption/desorption cycles under optimum conditions. The obtained results demonstrated that there is no obvious decrease in recoveries of analytes after four times of recycling indicating good reusability of the sorbent.

Method performance

Under the optimized extraction conditions, the analytical performance of the method in terms of enhancement factor (EF), limit of detection (LOD), linear dynamic range (LDR) and repeatability was evaluated. Results are summarized in Table 2. The calibration curves were constructed at ten different concentration levels by plotting the relative peak areas versus the concentration of the analytes. Two replicate extractions were performed for each concentration level. The calibration curves were linear within the range of 0.75–100 µg L⁻¹ with good coefficient of estimation ($R^2 > 0.998$). The repeatability of the method was evaluated by four replicate extractions of the spiked ultrapure water

samples with the analytes at 25 µg L⁻¹ level under the same operational conditions, and presented as the relative standard deviations (RSDs), which were between 2.9 % and 4.2 %, showing the good repeatability of the method. The enhancement factor was calculated by comparing the slopes of the calibration curves with and without preconcentration and was found to be 70–129. The LODs were calculated as $3S_b/m$ (S_b , standard deviation of the blank signals after extraction and m , slope of calibration curve of extraction), and found to be in the range of 0.2–2.0 µg L⁻¹.

A comparison of the MSPE-FI-ICP-OES method and some of the published methods for extraction and determination of the target metal ions are summarized in Table 3. Comparing to the other literatures, the linearity, limit of detection and precision of the method are comparable or better than the results of published methods. Also, the

Table 2 Analytical performance characteristics of the MSPE-FI-ICP-OES method for determination of target metal ions

Analyte	Linearity		LOD (µg L ⁻¹)	EF	Precision ^b (RSD%, $n=4$)
	LDR ^a (µg L ⁻¹)	R ²			
Ag ⁺	0.75–100	0.999	0.2	114	4.2
Au ³⁺	5.0–100	0.998	2.0	70	3.3
Cu ²⁺	1.0–100	0.999	0.5	129	2.9
Pd ²⁺	2.0–100	0.999	1.0	87	3.6

^a Linear dynamic range

^b Data were calculated based on the extraction of 25 µg L⁻¹ of each analyte

Table 3 Comparison of current method characteristics with those of previously developed methods for extraction and determination of target metal ions

Analyte	Extraction method	Detection system	LOD ($\mu\text{g L}^{-1}$)	LDR ($\mu\text{g L}^{-1}$)	RSD (%)	Ref.
Ag ⁺	SPE ^a	FAAS	8	–	<3	[3]
	MSPE ^b	ICP-OES	0.12	–	5.31	[20]
Au ³⁺	MSPE	ICP-OES	0.2	0.75–100	4.2	This work
	SPE	FAAS	16.6	–	<6	[17]
	SPE ^d	FAAS	0.1	0.45–10,000	2.3	[18]
Cu ²⁺	MSPE	ICP-OES	2.0	5.0–100	3.3	This work
	SPE ^c	FAAS	3.3	11–5,000	1.9	[19]
	MSPE ^b	ICP-OES	0.13	–	3.62	[20]
	IL-DLLME ^f	ICP-OES	0.1	5–200	3.4	[22]
	DLLME-SFO ^g	ICP-OES	0.2	1.25–250	6.7	[23]
Pd ²⁺	MSPE	ICP-OES	0.5	1.0–100	2.9	This work
	SPE ^h	Photoacoustic spectroscopy	4	12–210	<5	[7]
	IP-SAME ⁱ	ICP-OES	0.2	0.5–100	4.1	[21]
	MSPE	ICP-OES	1.0	2.0–100	3.6	This work

^a Based on chloromethylated polystyrene modified with 2-mercaptobenzothiazole

^b Based on magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propanol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole

^c Based on Amberlite XAD-2000 resin modified with diethyldithiocarbamate

^d Based on organo nanoclay modified with 5-(4'-dimethylamino benzylidene)-rhodanine

^e Based on ZrO₂/B₂O₃ nanosorbent

^f Ionic liquid based dispersive liquid-liquid microextraction

^g Dispersive liquid-liquid microextraction based on the solidification of floating organic drop

^h Based on cationic resin Dowex 50W X4 20/50 modified with 3-[2'-thiazolylazo]- 2,6 diaminopyridine (2,6 TADAP)

ⁱ Ion pair based surfactant-assisted microextraction

method does not need a chelating agent or organic solvent, is fast and selective.

Analysis of real samples

In order to evaluate the influence of the matrix on the performance of the method and to validate its accuracy and applicability, several water samples including tap water, river water

and two mineral waters were analyzed by the new method. The results are tabulated in Table 4. The results showed that the analyzed samples were free of three metal ions, Ag⁺, Au³⁺ and Pd²⁺ (at least below the detectable levels). However, Cu²⁺ was detected at all analyzed samples. Method accuracy was evaluated by means of recovery studies by spiking the real samples at concentration level of 10 $\mu\text{g L}^{-1}$ of Ag⁺ and Cu²⁺, and 20 $\mu\text{g L}^{-1}$ of Au³⁺ and Pd²⁺ ($n=3$). Satisfactory relative

Table 4 Results of determination of target metal ions in different real samples

Sample		Ag ⁺	Au ³⁺	Cu ²⁺	Pd ²⁺
Tap water	Found ($\mu\text{g L}^{-1}$)	<LOD	<LOD	11.9	<LOD
	RR (%)	106	109	107	110
	RSD (%)	5.6	7.2	6.8	5.7
Mineral water 1	Found ($\mu\text{g L}^{-1}$)	<LOD	<LOD	26.5	<LOD
	RR (%)	89	105	109	102
	RSD (%)	5.7	4.5	3.6	3.6
Mineral water 2	Found ($\mu\text{g L}^{-1}$)	<LOD	<LOD	7.1	<LOD
	RR (%)	98	88	103	88
	RSD (%)	3.3	9.4	4.8	4.5
River Water	Found ($\mu\text{g L}^{-1}$)	<LOD	<LOD	6.7	<LOD
	RR (%)	108	104	98	91
	RSD (%)	7.3	8.2	3.1	4.8

All samples were spiked at concentration level of 10 $\mu\text{g L}^{-1}$ of Ag⁺ and Cu²⁺, and 20 $\mu\text{g L}^{-1}$ of Au³⁺ and Pd²⁺

recoveries were obtained in all cases (88–110 %), with relative standard deviations (RSDs) in the range of 3.1–9.4 %, revealing that the matrices of the analyzed water samples had little effect on the performance of the method. It can be considered that the present method provides acceptable recoveries and precisions for the determination of these elements in real water samples.

Conclusions

In the present study, polythiophene coated Fe_3O_4 nanoparticles were synthesized and for a first time applied as a magnetic adsorbent for selective extraction of four metal ions. The main advantages of the developed approach is no consumption of chelating agent and organic solvents that is commonly used in complexation and extraction of metal ions, short analysis time (especially for large volume of samples) in comparison to conventional SPE sorbents, due to the high specific surface area, absence of internal diffusion resistance, operation in dispersion mode, and magnetic separation. With the characteristics of high selectivity, enhanced efficiency, good recoveries and precision, wide linearity, and great enrichment factor, MSPE-FI-ICP-OES method would provide an exciting low-cost and environmental friendly method for simple, selective and sensitive determination of Ag^+ , Au^{3+} , Cu^{2+} and Pd^{2+} ions in various real water samples.

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