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Use of Fe$_3$O$_4$ Magnetic Nanoparticles Coated with Polythiophene for Simultaneous Preconcentration of Cu (II), Co (II), Cd (II), Ni (II) and Zn(II) Ions Prior to their Determination by MIS-FAAS

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Abstract

A multielement preconcentration procedure based Fe$_3$O$_4$ magnetic nanoparticles coated with polythiophene(Fe$_3$O$_4$@ PTh MNPs) as a solid phase was reported for Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions. Following the preconcentration, the ions were determined by microsample injection system-flame atomic absorption spectrometer (MIS-FAAS). The effect of sample pH, type and volume of eluent, sample volume, extraction time, amount of adsorbent and interfering ions were optimized. The analytes were preconcentrated from 75 to 150 mL of sample solutions buffered to pH 7. The eluent was 1 mL of 1 mol L^{-1} HNO$_3$ solution. Under optimum conditions, the limits of detection for the analyte ions varied from 1 to 10 µg L^{-1}. The adsorption capacities of Fe$_3$O$_4$@PTh was in the range of 2.85 to 9.76 mg g^{-1}. The method was validated by analysis of the certified reference materials. The relative errors and standard deviations were lower than 5%. The developed procedure was applied to various water, soil and some vegetable samples.

Keyword: Fe$_3$O$_4$@PTh; heavy metals; preconcentration; water; vegetable; MIS-FAAS

1. Introduction

Large quantities of wastes containing toxic substances are discharged from various industrial plants into environment. Among these toxic substances, heavy metal ions such as Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) have an important place in environmental pollution. These metal ions merge with water and soil to threaten human life and health in food chain.[1] If concentrations in the environment exceed ppm levels, the metal ions exhibit toxic effects. Therefore, the concentrations of these heavy metal ions must be monitored carefully.

Many standard and reference methods have been designed for the determination of heavy metal ions at trace and ultratrace levels. Most commonly flame atomic absorption spectrometry (FAAS) is employed for the determination of trace heavy metals, due to its ease of operation, widespread availability, economical cost, and good precision. With FAAS, however, the direct determination of trace metal ions is difficult, because their concentrations are often lower than the limit of detection of FAAS and matrix problems can be encountered at very low concentrations. These difficulties can be overcome by applying a separation or preconcentration step like cloud point extraction, liquid–liquid extraction, coprecipitation and solid phase extraction, prior to their determinations by FAAS.[2–5]

The methods of solid phase extraction can be specified as disc, column and batch techniques. While these techniques allow working with large volume samples to achieve high preconcentration factor, they have limititations when samples contain insoluble suspending matter in aqueous media.[6] Column techniques are hindered due to slow percolation of samples through the column. In the disc and batch techiques, the solid phase in which the analytes are collected is contaminated with insoluble matters and proper separation does not occur. These limitations can be overcome by processes such as filtration and precipitation prior to preconcentration procedure, but the duration of the analysis is extended further. Magnetic solid

phase extraction technique (MSPE) has recently been suggested by Šafaříková and Šafařík as a new solid phase extraction technique developed for preventing these limitations.[7] Magnetic adsorbents are used in MSPE and they had been initially applied to preconcentration and separation of some organic dyes from various matrices. At MSPE, the small amount of magnetic solid phase where the analytes are adsorbed is effectively separated from the large volume sample solutions by means of a magnetic field. The analytes are eluted from the magnetic adsorbent by the appropriate volumes of eluent. The most commonly used magnetic sorbent is Fe_3O_4 (magnetite) due to its magnetic property. However, as a nanoparticle metal oxide it is not selective and is unstable in complicated matrices, especially at low pHs. Furthermore, metaloxide nanoparticles tend to aggregate in aqueous matrices, which decrease the efficiency of the method.[8,9] So, it is essential to coat its surface to avoid the aggregation and to gain selectivity. Polymer coated magnetic nanoparticles have been synthesized by coating the magnetic nanoparticle with polypyrrole,[10] polyaniline[11] and polythiophene[12,13] for extraction of organic or inorganic compounds from different matrices. Among these, the use of magnetic nanoparticles prepared with polythiophene is limited for magnetic solid phase extraction of trace metal ions.[14–17]

Herein, we prepared Fe_3O_4 magnetic nanoparticles coated with polythiophene (Fe_3O_4@PTh MNPs) as a magnetic solid phase for simultaneous preconcentration/separation of Cu(II), Co (II), Cd(II), Ni(II) and Zn(II) ions from various real samples such as some water, soil and vegetable samples prior to their determinations by MIS-FAAS. The important analytical variables affecting the MSPE procedure were optimized. The binding characteristics of Fe_3O_4@PTh for the analyte ions were evaluated using several adsorption isoterms. The method was validated with analysis of sample spiking analyte and the certified reference materials (CRMs) corresponding to the samples.

2. Experimental

2. 1. Instrumentation and Apparatus

A Perkin Elmer model AAnalyst 700 (Norwalk, CT, USA) flame atomic absorption spectrometer equipped with hollow cathode lamp, an air-acetylene burner and a hand-made microsample injection system (MIS) were used for the determination of metal ions. The microsample injection system reported in previous work allows acceptable absorbance to be obtained with a sample volume of 100 µL.[18] The spectral bandwidths were 0.7 nm for copper, cadmium and zinc, and 0.2 nm for cobalt and nickel. The acetylene flow rate and nebulizer flow rate were 2.5 and 10.0 mL min^{-1}, respectively. ATR-IR spectrometer (UATR two model from PerkinElmer) was used for recording ATR-Spectra. An analytical balance (Precisa XB-220A Switzerland), pH meter (WTW pH720, Weilheim, Germany), heating magnetic

stirrer (Velp Scientifica ARE, Usmate, Italy), dry air sterilizer (Nuve FN-055, Istanbul, Turkey), mini orbital shaker (VWR, USA) and ultrasonic bath (Ultrasound Bendelin Electronic, Berlin, Germany) were used.

2. 2. Reagents and Standard Solutions

All reagents used in the experiments were of the highest available purity and at least analytical reagent grade. Ultra pure (UP) quality water (resistivity 18.2 MΩ cm^{-1}) obtained from reverse osmosis system (Human Corporation, Seoul, Korea) was used for dilution and preparation of solutions. Nitric acid (65%), perchloric acid (70%), hydrochloric acid (37%), phosphoric acid(85%), acetic acid(glacial), sodium hyroxide, ammonia solution (25%), ethanol and hydrogen peroxide (30%) purchased from Merck, Darmstadt-Germany were used for wet digestion and pH adjustment of sample. Iron(III) chloride hexahydrate, iron(III) sulphate heptahydrate, potassium permanganate, anhydrous acetonitrile and thiophene used for the synthesis of polythiophene-coated Fe_3O_4 nanoparticles were supplied from Sigma-Aldrich, Steinheim-Germany.

Standard stock solutions of Cu(II), Cd(II), Co(II), Ni(II) and Zn(II) as 1000 mg L^{-1} were purchased from LGC, Manchester, USA, and further diluted daily prior to use. The pH of the model solutions was adjusted to pH 2 with $H_2PO_4^-$/H_3PO_4 buffer, pH 4–6 with CH_3COO^-/CH_3COOH buffer, pH 6.5–7.5 with $H_2PO_4^-$/HPO_4^{2-} buffer and pH 8–10 with NH_4^+/NH_3 buffer solutions. All glasswares used in experiments were kept in 20% (v/v) HNO_3 for at least 24 hours, and rinsed several times with ultra pure water prior to use.

2. 3. Synthesis of Polythiophene-Coated Fe_3O_4 Magnetic Nanoparticles

The synthesis of polythiophene coated Fe_3O_4 magnetic nanoparticles (Fe_3O_4@PTh MNPs) was performed with a small modification of previously published work.[12] Firstly, Fe_3O_4 MNPs was synthesized by co-precipitation method. For this, 8.48 g of $FeCl_3 \cdot 6H_2O$ and 3.15 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 400 mL UP water in a beaker heated at 80 °C, under protection of nitrogen gas, while vigorous stirring the beaker content at 1000 rpm by a magnetic stirrer. Then, 20 mL ammonia solution (25%, v/v) was added dropwise to the solution. The color of solution immediately turned from orange to black. After the mixture was stirred for a further 5 min, the Fe_3O_4 NPs precipitates formed was isolated by magnetic decantation using a neodium magnet and then rinsed several times with 100 mL UP water. The Fe_3O_4 NPs were dried in a vacuum oven at 70 °C for 10 h. The surface of Fe_3O_4 NPs were coated using polythiophene formed by oxidative polymerization of thiophene using $KMnO_4$. To do this, firstly, 1.0 g of dried Fe_3O_4 NPs dispersed in 10 mL anhydrous acetonitrile was sonicated with an ultrasonic bath for 10 min. Then,

1.5 mL of thiophene as the monomer was added to the Fe_3O_4 NPs suspension and then stirred by a magnetic stirrer in a beaker for 15 min. Thereafter, 50 mL of 0.6 mol L^{-1} KMnO$_4$ solution prepared in anhydrous acetonitrile was added drop by drop to the mixture stirred at 500 rpm. The final mixture was stirred for a further 3 h. Finally, synthesized Fe_3O_4@PTh MNPs was rinsed several times with UP water and ethanol, successively, and dried at 70 °C for 5 h under vacuum and then stored in a sealed vial in a desiccator before its use.

Fe_3O_4 surface coating with polythiophene was confirmed by the comparison of ATR-IR spectra of bare Fe_3O_4 (a) and synthesized Fe_3O_4@PTh (b) in Fig. S1. The strong peak at 545 cm^{-1} related to the Fe-O stretching vibration is confirmed the existence of Fe_3O_4 magnetic nanoparticles (Fig. S1a).[19] The peaks at 1561 ve 1419 cm^{-1} are attributed to C = C asymmetric and symmetrical stretching vibration of thiophene ring and the peaks at 700 and 800 cm^{-1} indicate the presence of C-S vibration bond of thiophene ring.[12]

2. 4. Preparation of Samples

The water samples such as tap water from our laboratory, mineral water purchased from a local supermarket, wastewater from Denizli wastewater treatment plant's outlet, thermal water from Pamukkale and hot spring water from Karahayıt, were collected around the city of Denizli, Turkey. The samples were filtered through a cellulose nitrate membrane filter of 0.45 μm pore size (Sartorius, Germany) and 50–150 mL aliquots of the filtered water samples transferred to a 250 mL beaker were buffered to pH 7 using a $H_2PO_4^-$/HPO_4^{2-} buffer. Then, the general procedure was applied to the prepared water samples.

The general procedure was validated analysing 0.5–2 mL aliquots of BCR 715 Industrial Effluent Wastewater and SPS-WW2 Batch 114 Wastewater as certified reference materials.

By modifying a recent literature,[20,21] 0.5 g of NCS DC 78302 Tibet Soil in a 50 mL beaker were digested for 6 h at 90 °C with 8 mL of aqua regia **(Aqua regia is highly corrosive and must be handled with extreme caution)** and 3 mL of concentrated HClO$_4$. Also, one gram of strawberry leaves was weighed in a small beaker and 4 mL of aqua regia were added. The mixture was heated for 3 h at 85 °C for the digestion of strawberry leaves. The digested residues of strawberry leaves and Tibet Soil were separately diluted to 5 and 10 mL with UP water, respectively and then filtered using the cellulose nitrate membrane filter. The filterates were analyzed by the general procedure described.

Vegetable samples including black radish, parsley and quince were purchased from open bazaar in Denizli, Turkey. The samples were thoroughly washed, first with tap water, followed by rinsing three times with UP water and homogenized using a blender, then dried in an oven at 80 °C for 48 h. The dried plant sample weighing 2.0 g was placed into a beaker and a mixture of 12 mL of concentrated HNO$_3$ (65%, v/v) and 4 mL of H$_2$O$_2$ (30%, v/v) was added to perform the digestion process for 4 h at 130 °C. Following completion of digestion process, the residue was cooled, diluted to 5 mL with UP water and finally filtered through 0.45 μm cellulose nitrate filter paper.[22] The filtrate was analyzed to determine the concentration of various elements using the proposed general procedure.

2. 5. General Procedure

The preconcentration of metal ions with MSPE were performed by batch technique. The preconcentration method was optimized using model solutions containing analytes in known quantities depending on the analyte before application of the method to real samples. Firstly, the model solutions were prepared varying concentration of analytes from 5.0 to 10.0 μg L^{-1} and then they were buffered to pH 7 using a $H_2PO_4^-$/HPO_4^{2-} buffer. Then, 100 mg of Fe_3O_4@PTh MNPs was separately added into 150 mL of Zn(II) solution, 125 mL of Cu(II), Co(II) and Ni(II) solutions and 75 mL of Cd(II) solution. The mixtures were shaken for 3 mins by hand. Fe_3O_4@PTh MNPs loaded with the analyte ions were separated from the mixtures by a neodymium magnet and the supernatant was discarded. The polythiophene-coated Fe_3O_4 MNPs loaded with copper(II), cobalt(II), cadmium(II), nickel(II) and zinc(II) ions were treated with 1 mL of 1 mol L^{-1} nitric acid for eluation. The obtained mixture was carefully shaken for 3 mins by hand. Then, the effluent including analyte ions was magnetically separated from the Fe_3O_4@PTh MNPs. 100 μL of the effluent was introduced into MIS-FAAS using a micropipette to determine the analytes.

3. Results and Discussion

The analytical variables affecting the MSPE procedure such as pH, type and volume of eluent, volume of sample, extractiom time, Fe_3O_4@PTh amount were optimized using a one-factor-at-a-time approach. All the experimental quantifications were evaluated as the average of at least three replicate measurements.

3. 1. Effect of pH

Researches involve the use of SPE, firstly, the pH of sample solution is examined as most important parameter affecting the extraction efficiency of solid phase. It may change the chemical structure of the adsorbent surface and the analyte. Therefore, the effect of pH on the recoveries of metal ions was investigated in pH range of 2–10 using buffered solutions. The pHs of test solutions containing 50 μg L^{-1} analyte ions were adjusted to pH 2 with $H_2PO_4^-$/H_3PO_4, pH 4–6 with CH_3COO^-/CH_3COOH, pH 6.5–7.5 with $H_2PO_4^-$/HPO_4^{2-} and pH 8–10 with NH_4^+/NH_3 buffer solutions. The test solutions were analyzed by general proce-

dure above and the calculated recoveries were plotted against pH (Fig. 1). The decrease in recovery values of analytes by the reduction of solution pH from 6.5 to 2 may be explained by the protonation of sulfur groups at functional site of polythiophene.[16] The protonation prevents the coordination of analyte ions by donor sulfur atoms, due to the electrostatic repulsion between the positive charged sorbent and the cationic analytes in acidic solution. On the other hand, because of the increasing hydrolysis and/or formation of ammine complexes of analyte ions at pHs 8 and 10 that were buffered with ammonium/ammonia, a slight decrease in the recovery value of analytes is observed. Around pH 7, because of decreasing protonation of the sulfur atoms and increasing formation of ammine complex of metal ions at pHs in the range of 6.5 and 7.5 that phosphate buffers were used, it can be concluded that more favorable conditions arise for interaction of analyte ions with the sulfur atoms at binding site of Fe_3O_4@PTh MNPs. Therefore, the quantitative recovery values($\geq$ 95%) are obtained in pH range of 6.5–7.5. As a result, pH 7 was chosen as the optimum working pH for further experiments. Also, the neutral pH was evaluated as an advantage for separation and preconcentration of trace metal ions from natural water samples without chemically pretreating the samples.
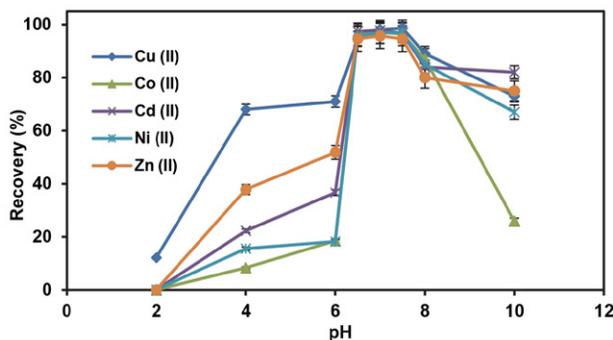

Figure 1. Effect of pH on the recoveries of the analyte ions (sample vol.: 20 mL, eluent vol.: 1 mL, n = 3)

3. 2. Effect of Concentration and Volume of Eluent

In SPE techniques, the volume of the eluent is usually chosen as low as possible to reach greater preconcentration factors along with having ecofriendly properties. It should also be sufficient for the quantitative extraction of the metal ions examined. So, the eluent choice is important. Based on Fig. 1, it was concluded that the recovery values decrease until under 10 % with decreasing pH values of the sample solution from 6.5 to 2.0 and the complex formation of metal ions with the donor atom (S) of Fe_3O_4@PTh will be largely prevented at the more acidic conditions. In this study, nitric acid as eluent was selected instead of hydrochloric acid to prevent the formation of chloro complexes of analyte ions. The concentration and volume of

HNO_3 were optimized for analysis. The quantitative recoveries ($\geq$95%) for Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions were obtained using 5 mL of HNO_3 solutions in the concentration range of 1–3 mol L^{-1} (Fig. 2). Then, 1.0 mol L^{-1} HNO_3 solutions in range of 1.0–10.0 mL were examined to achieve quantitative recoveries at minimum eluent volume (Table 1). To gain the highest sensitivity with the quantitative recovery values, 1.0 mL of 1.0 mol L^{-1} HNO_3 solution was used as eluent in further experiments.
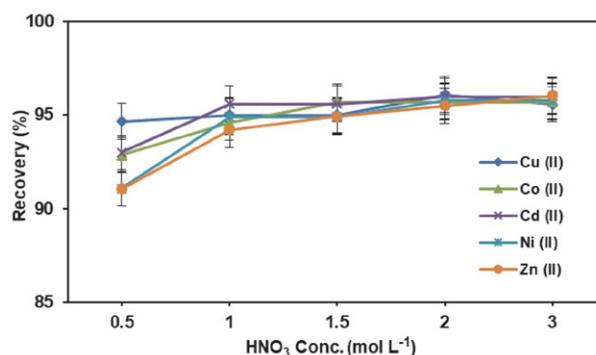

Figure 2. Effect of HNO_3 concentration on elution efficiency of Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions from 100 mg of Fe_3O_4@PTh MNPS (eluent vol.: 5.0 mL, n = 3)

Table 1. Effect of eluent volume on recovery of Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions (eluent: 1 mol L^{-1} HNO_3, n = 3)

Eluent Volume, mL	Recovery, %				
	Cu(II)	Co(II)	Cd(II)	Ni(II)	Zn(II)
10.0	96 ± 1	97 ± 3	98 ± 1	95 ± 2	96 ± 2
5.0	98 ± 1	96 ± 2	98 ± 1	96 ± 1	95 ± 1
2.5	97 ± 1	96 ± 2	96 ± 1	95 ± 2	96 ± 2
1.0	96 ± 2	95 ± 2	95 ± 1	95 ± 1	95 ± 2

3. 3. Effect of Sample Volume

Sample volume is chosen as large as possible to obtain high preconcentration factor in preconcentration studies. Therefore, the volume of the sample was investigated in the range of 10–200 mL solution, containing 5–10 μg L^{-1} of Cu(II), Co(II), Cd(II), Ni(II) and Zn(II). As shown in Fig. 3, it was found that the analyte ions could be adsorbed quantitatively when sample volumes were less than 150 mL for Zn(II) ions, 125 mL for Cu(II), Co(II) and Ni(II) ions, 75 mL for Cd(II) ions. The eluent volume used was 1 mL and the preconcentration factors (PF) were calculated to be 75 for Cd(II), 125 for Cu(II), Co(II) and Ni(II), and 150 for Zn(II).

3. 4. Effect of Extraction Time

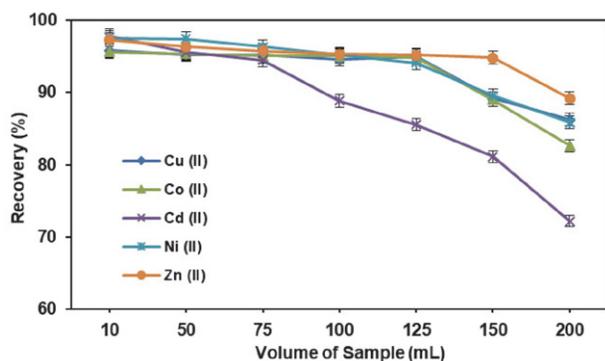The extraction time including adsorption and desorption times is defined as the minimum time required to

Figure 3. Effect of sample volume on the recovery of the analytes (Eluent vol.:1.0 mL, n = 3)

obtain quantitative extraction efficiency. Therefore, by changing the adsorption and desorption times between 1 and 20 min, the procedure was applied to a 50 mL sample solution containing analytes in the range of 5–10 µg L^{-1} and 100 mg $Fe_3O_4@PTh$. The results showed that 6 min extraction time as the sum of adsorption time (3 min) and desorption time (3 min) was adequate to access quantitative receovery for all analytes using 1.0 mL of eluent (Figures S2 and S3). It could be concluded that the extraction time is one of the most important advantages of magnetic solid phase extraction technique when compared with other solid phase extraction techniques such as column, filtration and batch.

3. 5. Effect of $Fe_3O_4@PTh$ Amount

To test the effect of $Fe_3O_4@PTh$ amount on recovery of analytes, the preconcentration procedure was applied to a 50 mL of sample solution including analyte ions in the range of 10–20 µg L^{-1} and $Fe_3O_4@PTh$ amount in the range of 30–250 mg. Based on the results depicted in Fig. 4, the recovery values for all the analyte were found to be quantitative(≥95%) using $Fe_3O_4@PTh$ in the range of 100–250 mg. 100 mg of $Fe_3O_4@PTh$ found to be as minimum amount that was preferred to minimize the risk of possible contamination.

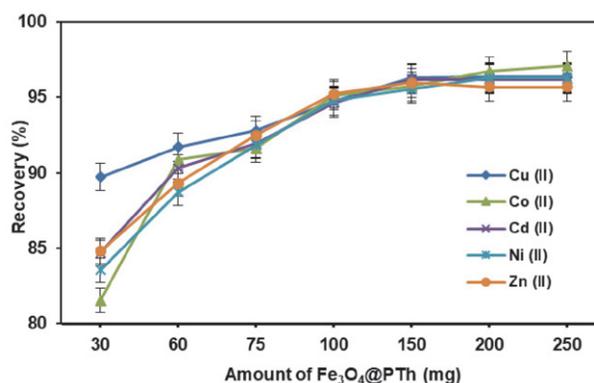**Figure 4.** Effect of the amount of the $Fe_3O_4@PTh$ on the recoveries of the analyte ions (n = 3)

Also, to evaluate the possibility of reuse of adsorbent, reusability tests were carried out by consecutive analysis under the optimum conditions. In the second use of $Fe_3O_4@PTh$, since the recovery values of all analytes are below 5%, it was concluded that the adsorbent can not be used more than once. Probably, on first use, the polythiophene from $Fe_3O_4@PTh$ is stripped during elution that limits its repeated use.

Table 2. Effect of interfering ions on the recoveries of the analyte ions (n = 3)

Interfering ions	Added as	Tolerance limits, mgL^{-1}	Recovery,%				
			Cu(II)	Co(II)	Cd(II)	Ni(II)	Zn(II)
Na$^+$	NaCl	4000	95 ± 1	95 ± 2	96 ± 1	96 ± 2	96 ± 2
K$^+$	KCl	5000	94 ± 1	95 ± 2	96 ± 1	95 ± 3	96 ± 1
Mg^{2+}	MgSO$_4$	2000	97 ± 1	94 ± 2	96 ± 1	95 ± 2	94 ± 1
Ca^{2+}	Ca(NO$_3$)$_2 \cdot$ 2H$_2$O	1000	95 ± 1	95 ± 2	95 ± 1	95 ± 2	95 ± 2
Ba^{2+}	BaCl$_2 \cdot$ 2H$_2$O	800	96 ± 1	95 ± 1	95 ± 2	95 ± 3	95 ± 2
Cl$^-$	NaCl	6174	95 ± 1	95 ± 2	96 ± 1	96 ± 2	96 ± 2
NO$_3^-$	Ca(NO$_3$)$_2 \cdot$ 2H$_2$O	6200	95 ± 1	94 ± 2	94 ± 1	94 ± 2	94 ± 2
CH$_3$COO$^-$	CH$_3$COONa $\cdot$ 3H$_2$O	4500	95 ± 1	94 ± 3	95 ± 2	96 ± 4	94 ± 1
CO$_3^{2-}$	Na$_2$CO$_3$	3500	94 ± 1	94 ± 3	95 ± 1	94 ± 4	94 ± 1
Cu^{2+}	CuCl$_2 \cdot$ 2H$_2$O	600	–	96 ± 2	94 ± 2	94 ± 2	95 ± 2
Pb^{2+}	Pb(NO$_3$)$_2$	500	96 ± 1	95 ± 2	94 ± 2	94 ± 3	94 ± 2
Ni$^+$	Ni(NO$_3$)$_2 \cdot$ 6H$_2$O	400	95 ± 1	94 ± 3	94 ± 1	–	94 ± 2
Cd^{2+}	Cd(NO$_3$)$_2 \cdot$ 4H$_2$O	500	95 ± 1	94 ± 3	–	94 ± 2	94 ± 2
Co^{2+}	Co(NO$_3$)$_2 \cdot$ 6H$_2$O	200	95 ± 1	–	95 ± 2	95 ± 2	95 ± 2
Zn^{2+}	Zn(NO$_3$)$_2 \cdot$ 6H$_2$O	500	95 ± 1	94 ± 2	96 ± 2	94 ± 3	–
Mn^{2+}	MnSO$_4 \cdot$ H$_2$O	300	94 ± 1	94 ± 2	94 ± 2	94 ± 2	94 ± 2
Cr^{3+}	Cr(NO$_3$)$_3 \cdot$ 9H$_2$O	300	95 ± 1	94 ± 2	94 ± 2	94 ± 3	94 ± 2
Fe^{3+}	Fe(NO$_3$)$_3 \cdot$ 9H$_2$O	80	94 ± 1	94 ± 2	94 ± 1	94 ± 2	94 ± 1

3. 6. Effect of Interfering Ions

During the application of the method, the selectivity of an adsorbent for an analyte ion can be hampered by interfering ions in the sample matrices. So, the selectivity of Fe_3O_4@PTh towards Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions in the presence of some interfering cations and anions was examined. The competitive adsorption effects of analyte ions on each other were also studied (Table 2). 50 mL of test solutions containing 100 μg L^{-1} of the each analyte ions were spiked with varying concentration of probable interfering ions, and then analysed by the proposed general procedure. The eluent volume used was 5.0 mL.

The tolerance limit was defined as the interfering ion concentration causing a deviation higher than 6% on the recovery values of the analyte ions. It was concluded that the proposed procedure could be applied successfully for the magnetic solid phase microextraction of Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) in presence of interfering ion at higher concentration than the concentration of matrix ions in samples. Also, the analytes have no significant interference on each other's extraction.

3. 7. Adsorption Capacity of Fe_3O_4@PTh

The adsorption capacity defined as the amount of adsorbent needed to quantitatively extract analyte ions in a sample solution is one of the important parameters.[23,24] To determine the adsorption capacity of Fe_3O_4@PTh for Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions, 50 mL sample solutions containing increasing initial concentrations (C_o) of analyte in the range of 5–500 mg L^{-1} that are buffered to pH 7 were contacted with 100 mg of adsorbent at room temperature for 24 h. The analyte ion concentrations in the supernatant solution diluted at the appropriate ratios were determined by FAAS. The procedure was separately repeated for each analyte ion. The adsorption capacities (Q_m) of Fe_3O_4@PTh MNPs for Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) were found to be 4.59, 4.88, 4.45, 2.85 and 9.76 mg g^{-1}, respectively, using Q_e values corresponding to the plateau in Fig. 5.
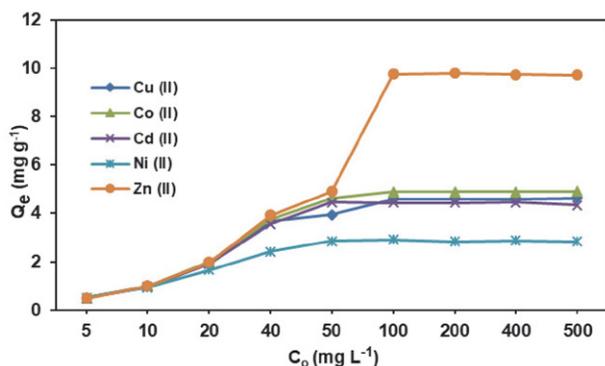

Figure 5. Adsorption capacity of Fe_3O_4@PTh for Cu(II), Co(II), Cd(II), Ni(II) and Zn(II)

The adsorption characteristics of Fe_3O_4@PTh MNPs were investigated using Langmuir, Freundlich, Scatchard, Temkin and Dubinin-Radushkevich isotherms and each isotherm calculation were applied to the experimental data(Table 3). The Langmiur isotherm equation is formulated as Ce/ Qe = 1/(Qm x Kb)+Ce/Qm, where Ce and Qe are equilibrium concentration of analyte ions(mg L^{-1}) in the solution and the solid phase (mg g^{-1}), respectively. The good regression coefficients ($R^2 \geq 0.9999$), R_L values in range of 0 and 1($R_L = 1/(1+K_b C_o)$) and Q_m values obtained from the isotherm close to the experimental adsorption capacities show the compatibility of the experimental data with the Langmuir isotherm. It can be concluded that the analytes on Fe_3O_4@PTh MNPs is favorably adsorbed with a monolayer adsorption process by the sites distribute uniformly.[25,26]

In the Freundlich isotherm equation given as ln Qe = lnKf + (1/n) lnCe, Kf and 1/n are Freundlich constants which corresponds to the adsorption capacity and adsorption intensity or heterogeneity of the adsorbent, respectively. The 1/n<1 and K_f values in Table 3, describe that all the analyte ions are favorably adsorbed by Fe_3O_4@PTh at low concentration.[25] The Scatchard isotherm defines the nature of binding sites and adsorption process. The equation is represented as $Q_e/C_e = Q_m x K_b - Q_e x K_b$, where K_b is the Scatchard isotherm constant. The shape of the isotherm plot explains the type of interaction between analyte ions and adsorbent. A good single linearity of the plot in working range verifies that the binding sites are equivalent and independent sites.[27] The concordance of Scatchard isotherm with experimental data is also supported with Q_m values close to the experimental adsorption capacities, low K_b and good R^2 values in Table 3. The Temkin isotherm given as $Q_e = A x lnK_T + A x lnC_e$ (A = RT/$b_T \cdot K_T$ (L g^{-1}) and b_T (J mol^{-1}) is the equilibrium binding constant and change of sorption energy, respectively. The high binding constants and high sorption energies of analytes indicate a strong interaction between the analyte ions and Fe_3O_4@PTh, supporting a chemisorption mechanism. The Dubinin-Raushkevich equation, generally used to distinguish between physical and chemical adsorption, is known as ln Qe = lnQm −K ε^2. ε value is formulated as ε = RTln(1+1/Ce). E(kJ/mol^{-1}) calculated from E = (−2K)$^{-1/2}$ is the mean free energy of adsorption per molecule of the adsorbate.[27] If the value of E lies between 8 and 16 kJ mol^{-1}, the adsorption process is a chemisorption, while values of below 8 kJmol^{-1} indicates a physical adsorption process.[28,29] The high adsorption energy values changed from 17.15 to 50.00 kJ mol^{-1} showed that the analytes were chemically adsorbed onto Fe_3O_4@PTh MNPs.

As a result, comparing the isotherms, it can be concluded that the values of R^2 and adsorption capacity obtained from Langmuir, Dubinin-Raushkevich and Scatchard isotherms are good fits to the experimental data. R^2 values of Freundlich and Temkin isotherms are relatively smaller than the others.

Table 3. Langmuir, Freundlich, Scatchard, Temkins and Temkin Dubinin–Radushkevich isotherm parameters for the adsorption of examined metal ions by Fe_3O_4@PTh

Isotherms	Parameters	Cu(II)	Co(II)	Cd(II)	Ni(II)	Zn(II)
Adsorption capacity	Q_m, mg g^{-1}	4.59	4.88	4.45	2.85	9.76
Langmiur	Q_m, mg g^{-1}	4.61	4.89	4.46	2.86	9.75
	K_b, L mg^{-1}	1.50	2.83	1.23	0.87	1.43
	R_L	0.12	0.066	0.14	0.19	0.12
	R^2	0.9999	1.0000	1.0000	0.9999	1.0000
Freundlich	K_f, L g^{-1}	2.13	2.90	1.55	1.22	2.13
	n	6.55	9.86	5.08	4.88	3.41
	R^2	0.9309	0.8714	0.8858	0.8618	0.8738
Scatchard	Q_m, mg g^{-1}	4.59	4.82	4.49	2.87	9.90
	K_b, L mg^{-1}	1.17	5.53	0.76	0.75	0.96
	R^2	0.9782	0.9355	0.9947	0.9696	0.9864
Temkin	K_T, L g^{-1}	13.79	97.89	89.20	96.05	37.60
	b_T, J mol^{-1}	2408	6093	5441	8570	2294
	B	1.0287	0.4066	0.4553	0.2891	1.0799
	R^2	0.9085	0.9204	0.8571	0.8949	0.9566
Dubinin – Radushkevich	q_s, mg g^{-1}	4.59	4.92	4.61	2.88	9.86
	K_{ad}, mol^2 kJ^{-2}	0.0004	0.0002	0.0005	0.0017	0.0004
	E, KJ mol^{-1}	35.36	50.00	31.62	17.15	35.36
	R^2	0.9892	0.9639	0.9935	0.9216	0.9959

3. 8. Method Validation

The method was validated in accordance with the guidelines set out in internationally accepted guidance documents. The validation's parameters, following the recommendations of the IUPAC and others, include limit of detection(LOD) and limit of quantification(LOQ), practical quantitation limit (PQL), linear range, precision, accuracy, selectivity, recovery and uncertainty of measurement.[30–33] The analytical figures of merit are summarized in Table 4. Due to the high experimental enrichment factors calculated

Table 4. Analytical characteristics of the proposed method at the optimum conditions.

Analytical characteristics	Cu(II)	Co(II)	Cd(II)	Ni(II)	Zn(II)
with reconcentration LR, µg L^{-1}	4–80	8–80	3–67	13–80	3–27
RE	y = 3.9579x + 0.0004	y = 3.2959x + 0.0014	y = 7.5124x + 0.0116	y = 3.0898x + 0.0072	y = 20.9775x + 0.0076
R^2	0.9996	0.9951	0.9963	0.9967	0.9994
without preconcentration LR, µg mL^{-1}	0.5–10	0.5–10	0.25–5	0.5–10	0.125-4
RE	y = 0.0325x + 0.0031	y = 0.0270x + 0.0044	y = 0.1039x + 0.0013	y = 0.0258x + 0.0067	y = 0.1454x + 0.0101
R^2	0.9994	0.9968	0.9981	0.9972	0.9985
Enrichment Factor	122	122	72	120	144
Preconcentration Factor	125	125	75	125	150
Error of EF, %	2	2	4	4	4
LOD (n = 16), µg L^{-1}	1.4	3.2	1.1	9.6	1.2
LOQ (n = 16), µg L^{-1}	3.6	5.1	1.9	11.7	2.6
PQL (n = 4), µg L^{-1}	4.0	8.0	3.2	13.2	3.3
Sample Vol., mL	125	125	75	125	150
Eluent Volume, mL	1	1	1	1	1
Consumptive index, mL	1.02	0.61	1.74	1.04	1.04

LR: Linear range; RE: Regression equation; R^2: Regression coefficient; EF: Enrichment Factor

Table 5. Analysis of certified reference materials using present method (n = 3)

Certified reference material		Cu(II)	Co(II)	Cd(II)	Ni(II)	Zn(II)
BCR 715	Certified, mgL^{-1}	0.90 ± 0.14[a]	–	0.040 ± 0.005	1.20 ± 0.09	4.0 ± 0.4
Industrial	Found, mg L^{-1}	0.86 ± 0.02	-	0.038 ± 0.001	1.16 ± 0.03	3.94 ± 0.05
Effluent	Recovery,%	96	–	95	97	99
Wastewater	RSD, %	2.3	–	2.6	2.6	1.3
	t$_{calculated}$ value	2.65[b]	–	3.50	2.00	1.89
SPS-WW2 Batch	Certified, mgL^{-1}	2.00 ± 0.01	0.300 ± 0.002	0.1000 ± 0.0005	5.000 ± 0.025	3.000 ± 0.015
114 Wastewater	Found, mg L^{-1}	1.93 ± 0.04	0.29 ± 0.01	0.095 ± 0.004	4.84 ± 0.14	2.88 ± 0.06
	Recovery, %	96	97	95	97	96
	RSD, %	2.1	3.3	4.2	2.9	2.1
	t$_{calculated}$ value	3.25	1.73	2.00	2.00	3.75
Tibet Soil	Certified, µg g^{-1}	24.6 ± 2.8	13.1 ± 1.1	0.081 ± 0.015	31.1 ± 1.6	58.0 ± 6.6
	Found, µg g^{-1}	23.19 ± 0.98	12.55 ± 0.54	0.078 ± 0.003	29.86 ± 0.62	54.98 ± 1.90
	Recovery, %	94	96	96	95	95
	RSD, %	4.2	4.3	3.8	2.1	3.5
	t$_{calculated}$ value	2.50	1.73	2.00	4.00	3.55
Strawberry Leaves	Certified, µg g^{-1}	10[c]	0.47 ± 0.11	0.17 ± 0.04	2.6 ± 0.7	24 ± 5
	Found, µg g^{-1}	9.09 ± 0.32	0.46 ± 0.02	0.16 ± 0.01	2.51 ± 0.15	22.95 ± 0.48
	Recovery, %	91	97	94	97	96
	RSD, %	3.5	4.3	6.2	6.0	2.1
	t$_{calculated}$ value	5.01	1.00	2.00	1.00	3.78

[a] Mean ± standard deviation; [b]Student's t-test, t$_{critical}$ = 4.30 at 95% confidence limit(N = 3); [c]not certified, but indicative value

as a ratio of the slopes of the regression equations established with and without the preconcentration, the sensivity of examined analytes determined with FAAS has been improved from trace level(µg mL^{-1}) to ultra trace level(µg L^{-1}), with very low enrichment error(≤ 4%). LOQ values for analytes (out of Ni) ranged from 1.1 to 3.2 µg L^{-1}. The quantitative recovery values (almost 95%) achieved in the analysis of certified reference materials and analyte spiked samples prove the accuracy of the proposed method (Tables 5, 6 and 7). The consumptive index[34] defined as the sample volume(mL) consumed to achieve a unit of EF was found to be quite low in Table 4. It is used to compare preconcentration procedures required different volumes of sample.

The accuracy of the developed procedure for each analyte was confirmed with analysis of the certified reference materials of wastewater (BCR715 and SPS-WW2 Batch 114), soil (NCS DC 78302 Tibet Soil) and plant (LGC7162 Strawberry Leaves). The recoveries and relative standard deviations(RSD,%) were calculated in the ranges of 91-99% and 1.3-6.2%, respectively. The certified and experimental values by applying Student's t-test were compared. The student t-test demonstrated that there is no significant difference between the certified value and the experimental result at the confidence level of 95%.[34] The results are shown in Table 5.

Precision of proposed method was evaluated as repeatability (intraday) and reproducibility (interday). These studies were carried out with analysis of samples spiked with analyte ions on four different days. All the experimental data were evaluated by one way analysis of variance (ANOVA).[35,36] Repeatability and reproducibility as relative standard deviations (RSD %) were in the range of 1.0–7.7% and 1.1–9.2%, respectively. Based on the results given in Table S1, there is no significant difference between the variances.

3. 9. Application of Proposed Method to Real Samples

To assess the applicability of the developed magnetic solid phase preconcentration procedure, it was applied to real samples spiked with analyte. The recoveries and relative standard deviations were obtained in the ranges of 93–97% and 0.7–2.9%, respectively(Table 6).

These recoveries confirm that the method is accurate and selective due to no interference from the sample matrices. The results showed that the actual water samples do not contain the analyte ions being studied (at least below limit of quantification). It was concluded that the proposed method has sufficient efficiency for the water samples including analyte ions at concentration higher than the LOQ values achieved by the proposed procedure.

The method was applied to some salad vegetables purchased from a local market in Denizli, Turkey. EU standards for the permissible levels of Cd(II) and Cu(II) are 0.2 and 20 mg kg^{-1}, respectively.[37] For Zn, permissible levels allowed by both EU standards and UK guidelines is

Table 6. Analysis of various water samples spiked with examined analytes (n = 3)

Ana-lyte	Added μg L⁻¹	Tap water Foundᵃ, μg L⁻¹	R, %	Mineral Water Foundᵃ, μg L⁻¹	R, %	Wastewater Foundᵃ, μg L⁻¹	R, %	Spring Water Foundᵃ, μg L⁻¹	R, %	Thermal Water Foundᵃ, μg L⁻¹	R, %
	0	< BLQᵇ	–	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–
Cu	10	9.5 ± 0.3	95	9.6 ± 0.2	96	9.5 ± 0.3	95	9.7 ± 0.3	96	9.7 ± 0.4	97
	20	18.9 ± 0.3	94	19.1 ± 0.3	96	18.8 ± 0.5	94	19.0 ± 0.3	95	19.1 ± 0.4	96
	0	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–
Co	10	9.4 ± 0.2	94	9.8 ± 0.2	98	9.4 ± 0.2	94	9.4 ± 0.2	94	9.6 ± 0.3	96
	20	18.7 ± 0.3	94	19.4 ± 0.5	97	18.7 ± 0.3	94	8.8 ± 0.2	94	19.0 ± 0.3	95
	0	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–
Cd	10	9.5 ± 0.2	95	9.7 ± 0.2	97	9.4 ± 0.1	94	9.5 ± 0.2	95	9.4 ± 0.1	94
	20	18.8 ± 0.2	94	19.2 ± 0.1	96	18.6 ± 0.2	93	18.6 ± 0.1	93	18.7 ± 0.1	94
	0	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–
Ni	20	19.1 ± 0.5	96	19.4 ± 0.5	97	18.7 ± 0.5	94	18.6 ± 0.5	93	19.0 ± 0.4	95
	40	37.7 ± 0.7	94	38.3 ± 0.5	96	37.5 ± 0.4	94	37.2 ± 0.5	93	37.6 ± 0.5	94
	0	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–	< BLQ	–
Zn	10	9.5 ± 0.1	95	9.8 ± 0.1	98	9.4 ± 0.1	94	9.4 ± 0.1	94	9.5 ± 0.1	95
	20	18.8 ± 0.2	94	19.3 ± 0.1	96	18.7 ± 0.2	94	18.7 ± 0.1	94	18.6 ± 0.1	93

ᵃ Mean ± standard deviation, ᵇ Below limit of quantification

50 mg kg⁻¹.[38–40] Standard concentration levels of Cd, Cr, Cu, Ni and Zn in vegetables are normally <0.5, 0.1–1, 2–20, 1–10 and 5–100 ppm, respectively.[41] Results indicated that the analyte concentrations in all the analysed vegetable samples are lower than the acceptable and the guidelines levels (Table 7). The recoveries were obtained in the ranges of 94–99%. The uncertainty of measurements are based on the uncertainty of calibration standard, calibration curve, adsorbent weighing, sample volume and repeatability and it is found to be in the range of 1.6–6.3%, depending the analyte(Table S2).[32,35]

3. 10. Comparison with Other Methods

The proposed method was compared to a variety of similiar preconcentration methods reported recently in the literature (Table 8). The method is more favorable than

the others, because it has higher enrichment factors, better precision, shorter extraction times (sum of adsorption and desorption times), and mild working conditions due to pH 7. While the LOD of this technique is not better than these other techniques, it does not require the costly equipment. Different experimental conditions used in this study allow extraction of analytes that cannot be extract by the reported method.[14] Another advantage of the method is the ability to simultaneously separate and preconcentrate more trace metals from real samples such as water, soil, fruit leaves and vegetable samples.

4. Conclusion

Using Fe₃O₄@PTh MNPs as magnetic adsorbent, a magnetic solid phase extraction method proposed for

Table 7. Analysis of some salad vegetables spiked with analyte ions (n = 4)

Analyte	Added, μg g⁻¹	Black Radish Root Foundedᵃ, μg g⁻¹	R, %	Parsley Foundedᵃ μg g⁻¹	R,, %	Quince Foundedᵃ μg g⁻¹	R, %
Cu(II)	0	0.55 ± 0.03	–	1.87 ± 0.08	–	2.55 ± 0.10	–
	0.5	1.00 ± 0.08	95	2.24 ± 0.06	94	2.90 ± 0.07	95
Co(II)	0	0.65 ± 0.06	–	0.94 ± 0.11	–	0.13 ± 0.02	–
	0.5	1.08 ± 0.07	95	1.36 ± 0.10	94	0.60 ± 0.06	96
Cd(II)	0	0.11 ± 0.01	–	0.24 ± 0.02	–	0.15 ± 0.01	–
	0.4	0.49 ± 0.03	96	0.61 ± 0.04	95	0.52 ± 0.03	94
Ni(II)	0	2.33 ± 0.08	–	1.93 ± 0.12	–	1.13 ± 0.06	–
	0.5	2.80 ± 0.12	99	2.30 ± 0.10	95	1.55 ± 0.10	95
Zn(II)	0	3.00 ± 0.12	–	3.26 ± 0.10	–	2.82 ± 0.07	–
	0.5	3.46 ± 0.11	99	3.58 ± 0.08	95	3.18 ± 0.05	96

ᵃ Mean ± standard deviation

Table 8. Comparative data from some recent studies based on use of the coated Fe_3O_4

Adsorbent/detection	Analytes	pH	Extraction	EF^b	LOD, Time^a	RSD,%	Refs. µg L^{-1}
Polythiophene@Fe_3O_4/ FI-ICP-OES	Cu	4	5 + 6	129	0.5	2.90	14
Polythiophene@Fe_3O_4 ETAAS	Cd	8	10 + 2	200	3.3	4.70	17
Polythionine@Fe_3O_4 / FAAS	Co	8	10 + 5	50	0.3	1.90	42
Carbon@Fe_3O_4/ ICP-MS	Co	5	10 + 5	37.5	0.001	9.40	
	Cd	5		37.5	0.055	6.20	43
	Zn	5		37.5	0.066	8.60	
	Pb	5		37.5	0.11	7.40	
Fe_3O_4@C-TAN/ FAAS	Cu	4	25 + 1	50	1.5	2.60	44
2-((E-2-amino-4,5-dinitrophenylimino)- methyl)-phenol@ SDS-coated Fe_3O_4/ FAAS	Pb	5	1 + −	63.5	0.04	2.8–3.6	45
Fe_3O_4@polythiophene/ FAAS	Cu	7	3 + 3	125	1	2.4	This work
	Co			125	3	2.4	
	Cd			75	1	1.7	
	Ni			125	10	2.3	
	Zn			150	1	1.5	

multielement preconcentration of Cu(II), Co(II), Cd(II), Ni(II) and Zn(II) ions prior to their determination by MIS-FAAS was successfully established. The method is green, simple, fast, and inexpensive in terms of chemicals, apparatus and manipulation. The method showed high performance including excellent accuracy, good precision, quantitative recovery, high enrichment factor and shorter extraction time for the analysis of samples having complex matrices such as waste water, soil and vegetable samples. These results are in accordance with those achieved by analysis of certified reference materials and real samples spiking analyte.

Conflict of Interest

Authors declare that they do not have any conflict of interest with anyone.

Acknowledgments

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Povzetek

V tem delu poročamo o večelementnem predkoncentracijskem postopku za ione Cu (II), Co (II), Cd (II), Ni (II) in Zn (II), ki je osnovan na Fe$_3$O$_4$ magnetnih nanodelcih, prevlečenih s politiofenom (Fe$_3$O$_4$ @ PTh MNPs) kot trdno fazo. Po predkoncentraciji smo ione določili z vbrizganjem mikro-vzorca v plamenski atomski absorpcijski spektrometer (MIS-FAAS). Optimizirani so bili vplivi pH vzorca, vrste in prostornine eluentov, prostornine vzorca, časa ekstrakcije, količine adsorbenta in motečih ionov. Analite smo predkoncentrirali od 75 na 150 ml in s pufrom uravnali pH na 7. Eluent je bil 1 ml raztopine HNO$_3$, koncentracije 1 mol L^{-1}. Pod optimalnimi pogoji so se meje zaznavanja ionov analita gibale med 1 in 10 μg L^{-1}. Adsorpcijska zmogljivost Fe$_3$O$_4$@PTh je bila v območju od 2,85 do 9,76 mg g^{-1}. Metoda je bila validirana z analizo certificiranih referenčnih materialov. Relativne napake in standardni odkloni so bili nižji od 5 %. Razviti postopek smo uporabili pri različnih vzorcih vode, zemlje in nekaterih rastlin.