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PAPER

Unmodified manganese ferrite nanoparticles as a new sorbent for solid-phase extraction of trace metal–APDC complexes followed by inductively coupled plasma mass spectrometry analysis

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The applicability of MnFe₂O₄ nanoparticles as a new sorbent for group pre-concentration of V, Co, Ni, Cu, Zn, As, Se, Cd and Pb was investigated and compared with that of magnetite nanoparticles. A solid-phase extraction (SPE) of target analytes based on sorption of their hydrophobic complexes with ammonium pyrrolidine dithiocarbamate (APDC) on the surface of unmodified nanoparticles (NPs) was optimized. Magnetic NPs with retained metal complexes were easily separated from the bulk solution by a permanent magnet applied for 5 min. Analyte restoration in the final solution was accomplished by heating with 0.5 mL of 7 mol L^{−1} nitric acid. The obtained solutions were suitable for continuous nebulization in ICP-MS. Spectral and non-spectral matrix effects for urine analysis (direct and after SPE) were studied and adequate calibration strategies are suggested. Under optimized conditions the magnetically assisted SPE procedure enables enrichment of target analytes by factors of between 7.4 and 10, with linear dynamic ranges of 1–100 µg L^{−1} for V, Co, Ni, Cd, Pb and 10–1000 µg L^{−1} for Zn, As, Se and method detection limits in the interval 0.01–0.7 µg L^{−1}. The relative standard deviations (RSD%, for 10 µg L^{−1} V, Co, Ni, Cd, Pb and for 100 µg L^{−1} Zn, As, Se, *n* = 6) were less than 5.5%. The accuracy of the method was evaluated by analysing urine certified reference material Seronorm™ Trace Elements Urine 201205 and obtained recoveries were in the range 85–109%. For correct determination of As and Se in urine, a preliminary microwave sample treatment with a mixture HNO₃ + H₂O₂ was needed, but it led to a worsening of method detection limits. The developed method was successfully applied for analysis of human urine.

1. Introduction

The use of magnetic nanoparticles (NPs) for solid-phase extraction (SPE) is promising because of their high surface area to volume ratio.^{1–5} The superparamagnetic properties of NPs in most cases have been exploited for a quick separation of dispersed sorbents from sample solutions by means of an external magnetic field as well as for controllable packing of micro-columns^{6,7} or micro-channels in lab-on-chip systems.⁸

Iron oxides such as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have been mostly applied as sorbents in organic analysis of hydrophobic compounds^{2,9} or for water purification.^{10–14}

Most of the published methods in the field of trace element analysis also deal with sorbent Fe₃O₄ NPs.^{6–8,15–27} They were successfully applied for separation/pre-concentration of trace

elements from water,^{7,15–17,20–22,25–27} seawater,^{6,18,19} biological,^{8,15,18,22,27} urine⁶ and food²⁴ samples.

The combination of SPE with magnetite NPs and plasma spectrometry methods has been described in some papers as ICP-OES,^{17,22,25,26} ICP-MS^{18–20} and ETV-ICP-MS.⁸ Nevertheless in our opinion more detailed examination of matrix effects and compatibility of the solutions obtained after SPE with inductively coupled plasma is helpful to extend the potential of magnetically assisted SPE-ICP-MS.

Usually when magnetic NPs are applied for pre-concentration, their surface is modified with silica.^{8,18–21} This ensures the protection of magnetite in acidic media, decreases the agglomeration propensity and gives the possibility for additional bonding of complexing agents, but at the expense of loss of magnetic properties.¹ Moreover Karatapanis *et al.*²¹ stressed the need to use an extra layer of cationic surfactant on Fe₃O₄ NPs already modified with silica. Thus, the authors achieved quantitative sorption of Pb and Cd complexes with 8-hydroxyquinoline, but the preparation of adsorbent was complicated significantly.

Two approaches were used for analyte retention on the surface of modified nanoparticles: chemical bonding with active groups

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linked on the sorbent surface^{1,6,18–20,22–27} or complex formation in a bulk solution^{16,17,21} followed by sorption.

To the best of our knowledge, the sorption of hydrophobic metal complexes, previously formed in a sample solution, on unmodified surfaces of magnetic NPs has not been studied so far.

In previous studies well-known reagents such as poly(acrylic acid) (PAA),⁶ dithizone,¹⁵ 1-(2-pyridylazo)-2-naphthol (PAN),^{17,24,25} γ -mercaptopropyltrimethoxysilane^{18,19} and morin^{22,23} were applied as ligands.

Ammonium pyrrolidine dithiocarbamate (APDC) is also a popular chelating agent capable of forming very stable hydrophobic complexes with more than 40 metal ions.²⁸ It was used in a variety of pre-concentration techniques such as co-precipitation²⁸ and SPE,^{29,30} liquid–liquid extraction³¹ and cloud point extraction.^{32,33} APDC was successfully combined with some nanosized materials for SPE. The retention of hydrophobic metal chelates onto multiwalled carbon nanotubes was used for pre-concentration of Cu, Cd, Pb, Zn, Ni and Co ions³⁴ as well as for speciation analysis of Cr³⁺ prior to FAAS analysis. Silver NPs attached to silica gel and impregnated with APDC were used for determination of lead in waters by FAAS.³⁶ In this work we tested the combination of magnetic NPs with APDC which has not been studied for SPE of trace elements until now.

Recently the sorption and magnetic properties of different types of substituted ferrites with the common formula MeFe_2O_4 (Me = Mn, Mg, Zn, Cu, Ni and Co) were studied.^{37–39} Hu *et al.*³⁷ showed that MnFe_2O_4 nanoparticles have the strongest magnetic properties and the highest surface area among all the studied ferrites. The utilisation of manganese ferrite NPs for SPE of trace elements has not been studied yet, despite their potential mentioned above.

This paper describes the applicability of unmodified MnFe_2O_4 NPs for simultaneous pre-concentration of V, Co, Ni, Cu, Zn, As, Se, Cd and Pb complexes with APDC. The parameters of SPE obtained with the new sorbent are compared with those obtained with well-studied Fe_3O_4 NPs. The optimized SPE procedure was tested for ICP-MS analysis of trace elements in human urine.

2. Experimental

2.1. Instrumentation

An inductively coupled plasma quadrupole mass spectrometer (Agilent 7700, Tokyo, Japan) with an octopole reaction system (He collision gas flow of 4.8 mL min^{-1}) was used for optimization studies and for analysis of urine samples – direct and after SPE. The instrumental parameters were as follows: RF power: 1.5 kW; plasma, auxiliary and nebulizer Ar gas flow rates: 15 L min^{-1} , 0.9 L min^{-1} and 0.95 L min^{-1} respectively; sample flow rate: 0.34 mL min^{-1} . Fifteen isotopes – ^{51}V , ^{59}Co , ^{60}Ni , $^{63,65}\text{Cu}$, $^{66,68}\text{Zn}$, ^{75}As , $^{77,82}\text{Se}$, $^{111,114}\text{Cd}$, $^{206,208}\text{Pb}$ and ^{103}Rh (as internal standard) – were monitored with 100 ms dwell time and five replicates were measured.

For size and shape characterization of magnetic NPs a JEM-2010 high-resolution transmission electron microscopy (HR-TEM) instrument (JEOL Ltd, Tokyo, Japan) coupled to an Inca Energy TEM100 energy dispersive X-ray spectrometer (EDS) (Oxford Instruments, Marlow, UK) was used.

A microwave system (MDS-81D, CEM Corp., Indian Trail, NC, USA) was used for the treatment of urine samples.

2.2. Reagents and samples

All reagents were of analytical or suprapur reagent grade. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and $\text{Mn}(\text{NO}_3)_2$, used for NP synthesis, and the complexing agent (APDC) were purchased from Sigma Aldrich Company (Milwaukee, WI, USA). Other reagents including NaOH, ammonia solution (NH_3) 25% for magnetic NP precipitation and HNO_3 65% suprapur for elution were from Merck (Darmstadt, Germany). Double-distilled water was used for the preparation of all solutions.

ICP multi-element standard solution VI (Merck, Darmstadt, Germany), after appropriate dilution, was used as a model solution for SPE procedure optimization as well as for the preparation of calibration standards. A single-element solution of Rh (10 mg L^{-1} , Fluka Chemie GmbH, Buchs, Switzerland) was tested as internal standard candidate.

The urine certified reference material Seronorm™ Trace Elements Urine 201205 (SERO AS, Billingstad, Norway) was used for the validation of the SPE procedure.

The human urine was collected from a laboratory worker.

2.3. Magnetic NP synthesis

The magnetic NPs were produced by co-precipitation of a mixture containing Me^{2+} ions ($\text{Me}^{2+} = \text{Mn}^{2+}$ or Fe^{2+}) and Fe^{3+} keeping a constant molar ratio of 1 : 2 ($0.017 \text{ mol L}^{-1} \text{ Me}^{2+} : 0.034 \text{ mol L}^{-1} \text{ Fe}^{3+}$ in a volume of 500 mL) in basic media. The synthesis of MnFe_2O_4 was performed by adding 350 mL of 0.25 mol L^{-1} NaOH at once to the precursor solution heated at 30°C . Then the temperature was increased up to 80°C and kept there for 3 hours.

The synthesis of Fe_3O_4 NPs was done by precipitation with 0.25 mol L^{-1} ammonia solution (500 mL), added at once to the precursor solution at ambient temperature and stirred for 30 min.

The magnetic NPs were separated from the supernatant solution by means of an external magnet and washed with double-distilled water until the washing solution reached $\text{pH} = 7$ then once more with $\sim 50 \text{ mL}$ of ethanol. Produced NPs were stored as suspensions in double-distilled water and were stable up to 6 months for MnFe_2O_4 and up to 1 month in the case of Fe_3O_4 NPs.

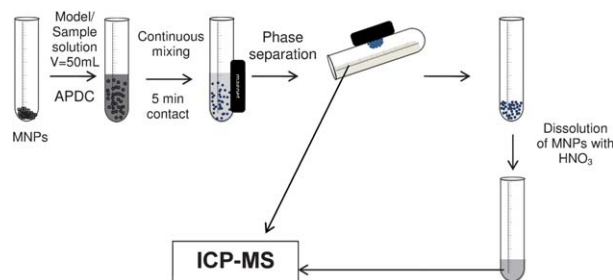


Fig. 1 Magnetic NP (MNP)-based SPE procedure.

2.4. Magnetic NP-based solid-phase extraction

The SPE procedure was performed in batch mode as presented in Fig. 1. The optimization of SPE was carried out using model solutions prepared by dilution of a multi-element standard.

Approximately 5 mg of the MnFe_2O_4 NPs (or 10 mg of Fe_3O_4) were transferred into a conical test tube ($V = 50$ mL). Afterwards a 3 mL solution of APDC with concentration of 2% m/v (corresponding to 60 mg of complexing agent) and sample solution were added, and then the pH was adjusted to 4. The extraction of metal chelates was performed by continuous shaking for 5 min.

MnFe_2O_4 NPs with the adsorbed metal complexes were separated by a permanent magnet applied for 5 min (10 min for Fe_3O_4), and the supernatant solution was decanted. The isolated solid phase was washed with 10 mL of double-distilled water.

The analyte restoration in final solutions was done by treatment with nitric acid in a boiling water bath as follows: MnFe_2O_4 was heated for 20 min with 0.5 mL of 7 mol L^{-1} nitric acid while Fe_3O_4 was heated for 15 min in 0.5 mL of 5 mol L^{-1} nitric acid. Under these conditions the MnFe_2O_4 NPs were partially dissolved, while magnetite NPs were completely dissolved. The obtained solutions were additionally diluted up to 5 mL and subjected to ICP-MS analysis.

2.5. Sample preparation

Lyophilized reference material was restored according to the procedure recommended by the manufacturer (in order to obtain 20 mL solution). Two alternative treatments of the certified reference material (CRM) were compared prior the SPE procedure. The solutions were spiked with 4 mL of (i) HNO_3 or (ii) a mixture of $\text{HNO}_3 : \text{H}_2\text{O}_2 = 3 : 1$, and then irradiated in a microwave (MW) oven for 20 min at 600 W. The clear digests were transferred to plastic tubes and after adjustment to $\text{pH} = 4$ (with ammonia solution) were diluted to a final volume with water. Blank samples were prepared as well.

The human urine sample was centrifuged at 4000 rpm for 10 min prior to analysis. To 50 mL of urine sample 10 mL of HNO_3 (65%) were added and the solution was subjected to MW treatment for 20 min at 600 W. The urine was transferred to a volumetric flask and diluted up to 100 mL. A blank sample was prepared as well.

2.6. Calibration strategies and sample analysis

The CRM solutions and urine sample prepared as described above were subjected to the SPE procedure (see Section 2.4). For the SPE procedure two calibration strategies were compared: (i) SPE calibration, where aqueous calibration standards were subjected to the same SPE procedure as samples (SPE calib) and (ii) the method of standard addition where two spikes (with final concentrations of $5 \mu\text{g L}^{-1}$ and $10 \mu\text{g L}^{-1}$ for V, Co, Ni, Cu, Cd, Pb and $50 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$ for Zn, As, Se) were added to the sample aliquot before SPE (Urine SPE StAdd).

For direct ICP-MS analysis the urine samples were diluted to final dilution factor (DF) = 10. The method of standard addition (StAdd) was applied to correct a non-spectral matrix effect. Two spikes from the multi-elemental standard solution were added to the urine sample.

3. Results and discussion

The aim of the current study was to investigate the potential of manganese ferrite NPs as a new sorbent for SPE of trace elements. To distinguish the specific behaviour of MnFe_2O_4 parallel investigations were made with the most often used NPs – Fe_3O_4 .

3.1. Magnetic nanoparticle characterization

The produced magnetic NPs were characterized by HR-TEM (Fig. 2A and B). In the case of MnFe_2O_4 NPs two fractions with mean diameters ~ 2 nm and ~ 20 nm could be distinguished, while the distribution of Fe_3O_4 particles was monomodal with a mean diameter ~ 14 nm (Fig. 2C and D). It was confirmed by EDS analysis that manganese ferrite had the desired molar ratio $\text{Mn} : \text{Fe} = 1 : 2$. Since the synthesis procedure and the size of produced MnFe_2O_4 NPs are similar to those reported by Hu *et al.*,³⁷ we expect that the other physical characteristics (*i.e.* BET surface area and magnetic properties) also should be comparable. Therefore, fine manganese ferrite NPs were synthesized successfully and their potential as a sorbent for SPE was studied further.

3.2. Optimization of ICP-MS detection method

During this study three different solutions were subjected to ICP-MS analysis (Fig. 1): (i) residual aqueous phase after extraction, (ii) final solution obtained after SPE and (iii) urine sample (for direct analysis).

The matrix effects (spectral and non-spectral) were examined in all three cases and different correction approaches were tested.

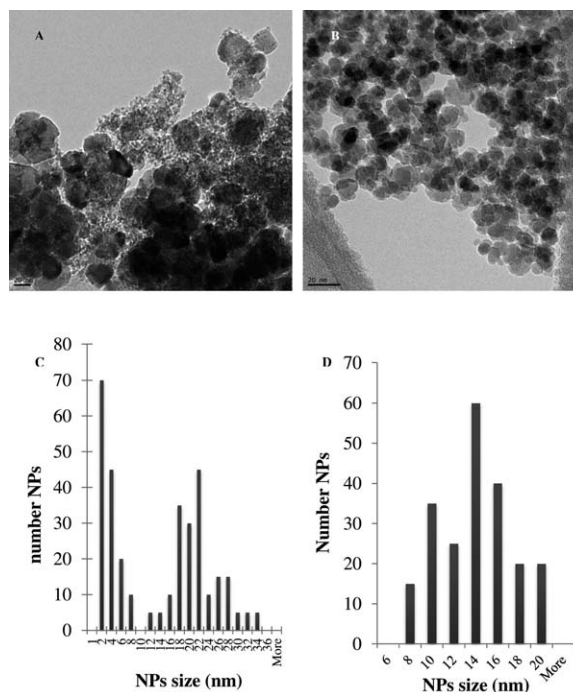


Fig. 2 TEM images of produced NPs with corresponding size distribution diagrams for MnFe_2O_4 (A and C) and Fe_3O_4 (B and D).

For the estimation of spectral interferences two isotopes per element were monitored and/or He collision mode was used. Isotopes free from isobaric overlap were selected, *i.e.* $^{60,62}\text{Ni}$, $^{63,65}\text{Cu}$, $^{66,68}\text{Zn}$, $^{111,114}\text{Cd}$ and $^{206,208}\text{Pb}$. For monoisotopic elements ^{59}Co and ^{75}As a second measurement with a collision cell was made. Vanadium has only one free isotope, ^{51}V , which was also measured in collision mode.

The measurements of both residual aqueous phase and final solutions obtained after SPE were free of spectral interferences, so the isotope with higher natural abundance was quantified without the need of collision gas.

When direct analysis of urine samples was performed, considerable spectral interferences on ^{51}V , ^{63}Cu and ^{75}As were registered due to formation of polyatomic ions from $^{35}\text{Cl}^{16}\text{O}^+$, $^{40}\text{Ar}^{23}\text{Na}^+$ and $^{35}\text{Cl}^{40}\text{Ar}^+$ respectively. Hence, the measurement in He mode is strongly recommended for V and As while the free ^{65}Cu isotope was preferred.

The non-spectral matrix effect was evaluated by comparison of sensitivities in each sample solution to the external calibration using common aqueous standard solutions stabilized with $0.07 \text{ mol L}^{-1} \text{ HNO}_3$ (eqn (1)).

$$\text{Matrix effect}\% = (\text{Sens}_{\text{Matrix}} - \text{Sens}_{\text{Aq.Std}}) \times 100 / \text{Sens}_{\text{Aq.Std}} \quad (1)$$

where: $\text{Sens}_{\text{Matrix}}$ is the slope of the calibration line in the presence of the studied matrix; $\text{Sens}_{\text{Aq.Std}}$ is the slope of the calibration line obtained using aqueous standards.

Up to 10% signal suppression due to the ligand (APDC) remaining in the aqueous phase was observed when residual analyte concentrations were measured. The matrix effect can be compensated with internal standard ^{103}Rh .

The matrix effect caused by components in the final solutions after SPE was studied as well. Here the overall matrix effect could be attributed to both the higher concentration of nitric acid (0.7 or 0.5 mol L^{-1}) as well as to the matrix derived from dissolved NPs.

Both effects were evaluated separately. Weak signal suppression in the range 7–12% caused by nitric acid was found only for Co, V, Zn, As and Se. The partially dissolved MnFe_2O_4 NPs caused more serious matrix suppression (in the range –14% to –27%) for all studied elements (Fig. 3). However, the loss of

sensitivity due to the manganese ferrite matrix is almost two times less than that observed for the Fe_3O_4 matrix (–30 to –40%).

As shown in Fig. 3, the suppression is not strictly element specific and hence a single internal standard could efficiently compensate for the matrix effect. Significant reduction of the matrix effect for all target analytes (from +4% for Cd and Pb to –9% for Ni) was obtained by applying internal standard ^{103}Rh .

The best strategy to overcome the matrix effect is to calibrate with standards prepared in the same medium as the sample. This was tested in two ways: (i) standards were spiked in a procedural blank (matrix matched calibration) and (ii) the aqueous standards were subjected to the SPE procedure (SPE calibration).

It should be noted that with continuous introduction of final solutions obtained after SPE a long-term drift of ICP-MS signals was observed, but it was less pronounced for the manganese ferrite matrix. The method of internal standardization is helpful in correction of instrumental drift; therefore it was used for all the measurements in the current study.

The only case of element-specific signal suppression was observed during the direct measurement of dilute urine. Here the matrix-induced sensitivity change varied from slightly positive for As and Se (up to +5%), to negative for Zn and Pb (–24%). Therefore the method of standard addition should be used as a calibration strategy for correction of different element behaviours for direct urine analysis by ICP-MS.

3.3. Optimization of SPE

During the optimization of the SPE procedure, the studied parameters are divided into two groups: (i) parameters influencing the complex formation reaction (metal ions with APDC) and (ii) parameters affecting the sorption/desorption of hydrophobic complexes on the surface of NPs.

The extraction degree $E\%$ (eqn (2)) was used for the optimization of pH and ligand and NP quantity. For calculation of $E\%$, model solutions (with known initial analyte concentrations) were subjected to SPE and the concentration of elements in residual aqueous phase was measured by ICP-MS.

$$E\% = (Q_{\text{initial}} - Q_{\text{residual}}) \times 100 / Q_{\text{initial}} \quad (2)$$

where: $E\%$ is the extraction degree; Q_{initial} is the analyte quantity in the model solution; Q_{residual} is the final analyte quantity in residual aqueous phase after SPE.

The recovery ($R\%$) was used for the assessment of the desorption procedure (eqn (3)). In this case the solid phase separated after SPE (containing magnetic NPs with collected metal-APDC complexes) was treated additionally to restore analytes in the solution and their concentrations were measured by ICP-MS.

$$R\% = Q_{\text{SPE}} \times 100 / Q_{\text{initial}} \quad (3)$$

where: $R\%$ is the recovery; Q_{initial} is the analyte quantity in the model solution; Q_{SPE} is the analyte quantity obtained after the SPE procedure.

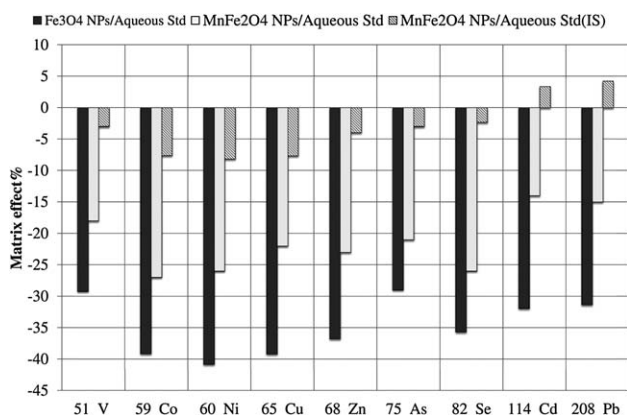


Fig. 3 Non-spectral matrix effect in final solutions after SPE, normalised (in %) to the external calibration using aqueous standards.

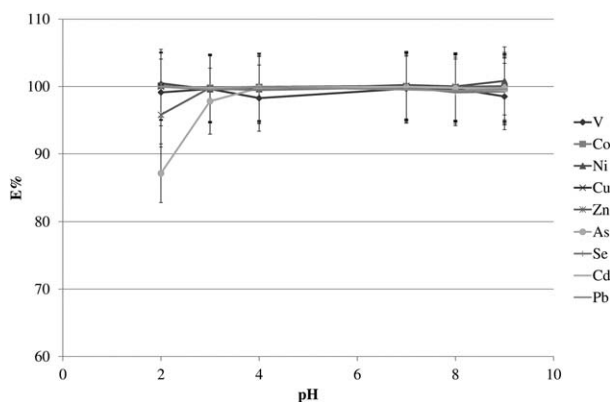


Fig. 4 Effect of solution pH on the extraction degree of metal complexes with APDC on MnFe_2O_4 NPs. Other conditions: 10 mg NPs; 60 mg APDC; $C_A = 100 \mu\text{g L}^{-1}$ for V, Co, Ni, Cu, Cd, Pb and $1000 \mu\text{g L}^{-1}$ for Zn, As, Se; $V_A = 50 \text{ mL}$.

3.3.1. Study of pH influence on extraction degree. The solution pH is a parameter influencing the formation of Me–APDC chelates and the sorption efficiency of hydrophobic complexes on magnetic NP surface.

The effect of pH on the extraction degree of target metal ions was assessed in the pH range from 2 to 9 (Fig. 4). The pH was adjusted by addition of ammonia solution or nitric acid, in the presence of ligand. As seen from Fig. 4, quantitative extraction ($E\% > 98$) was obtained for all studied elements in the whole range of pH (with the exception of As at pH = 2). Considering the fact that APCD can be partially degraded in strongly acidic solutions, pH = 4 was selected for all further experiments.

3.3.2. Optimization of APDC quantity. The effect of the amount of APDC on the extraction efficiency was studied by varying the quantity of ligand added to the model solution between 0 and 360 mg. Fig. 5 shows the extraction degree of the studied elements *versus* quantity of complexing reagent. Obviously sorption of target analytes on the NP surface is not possible without the complexation reaction, with the exception of V

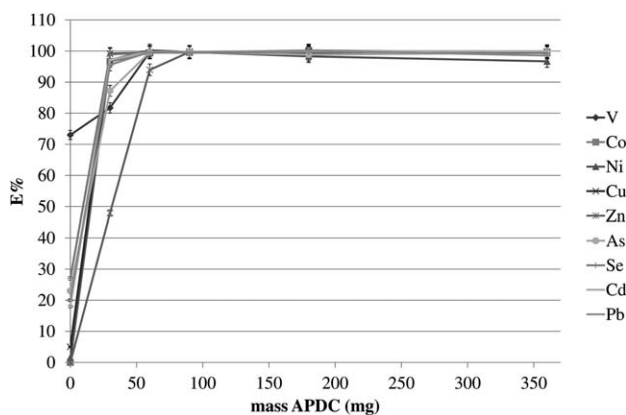


Fig. 5 Effect of the amount of complexing reagent (APDC) on the extraction degree of the studied elements on MnFe_2O_4 NPs. Other conditions: pH = 4; 10 mg NPs; $C_A = 100 \mu\text{g L}^{-1}$ for V, Co, Ni, Cu, Cd, Pb and $1000 \mu\text{g L}^{-1}$ for Zn, As, Se; $V_A = 50 \text{ mL}$.

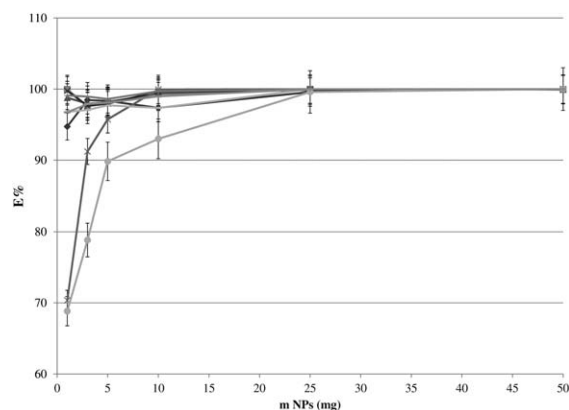


Fig. 6 Effect of the amount of sorbent on the extraction degree of metal complexes with APDC for MnFe_2O_4 NPs. Other conditions: pH = 4; 60 mg APDC; $C_A = 100 \mu\text{g L}^{-1}$ for V, Co, Ni, Cu, Cd, Pb and $1000 \mu\text{g L}^{-1}$ for Zn, As, Se; $V_A = 50 \text{ mL}$.

($E\% \sim 70$) and As ($E\% \sim 25$). All examined elements were quantitatively extracted ($E\% > 95$) when at least 60 mg of APDC were added to 50 mL of model solution containing 5 μg of V, Co, Ni, Cu, Cd, Pb and 50 μg of As, Se, Zn.

3.3.3. Optimization of amount of sorbent and time for separation. In comparison to common sorbents used in SPE, the NPs possess significantly higher surface area, and therefore the amount of sorbent needed for quantitative extraction of analytes is significantly lower. In addition, the surface-to-volume ratio of MnFe_2O_4 NPs is higher than that of magnetite.³⁷ The quantity of MnFe_2O_4 NPs was varied at levels of 1, 3, 5, 10, 25 and 50 mg (Fig. 6).

Extraction degrees higher than 90% were achieved using only 3 mg of NPs. Further experiments were performed with 5 mg of manganese ferrite NPs, because for all analytes $E \geq 95\%$ was obtained with the exception of As.

The time for complete separation of magnetic NPs from a bulk solution is dependent on the size of the NPs, their magnetic properties and the sample volume. Here the time was investigated using conical test tubes containing 50 mL of sample and

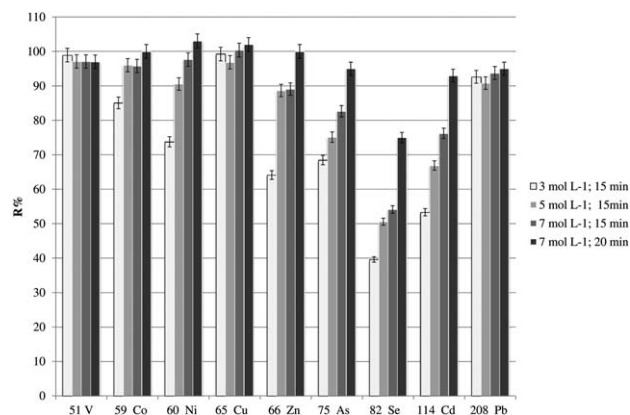


Fig. 7 Recoveries obtained for studied analytes after restoration. Other conditions: pH = 4; 5 mg MnFe_2O_4 NPs; 60 mg APDC; $C_A = 10 \mu\text{g L}^{-1}$ for V, Co, Ni, Cu, Cd, Pb and $100 \mu\text{g L}^{-1}$ for Zn, As, Se; $V_A = 50 \text{ mL}$.

5 mg of magnetic NPs. In the case of MnFe_2O_4 the solution becomes clear after ≈ 5 min.

3.3.4. Study of the analyte restoration procedure. Different types of reagents such as organic solvents,⁴⁰ combination of nitric acid and acetone^{34,41} or nitric acid alone⁴² were proposed as common eluents for desorption of the retained Me–APDC complexes from the solid phase. Considering the final instrumental detection chosen in this work, namely ICP-MS, the introduction of organic solvents is not an appropriate choice. Therefore only the elution of Me–APDC chelates with nitric acid (in the concentration range 3–7 mol L^{−1}) is studied. The efficiency of restoration is assessed by analyte recovery – $R\%$ (eqn (3)).

Incomplete recoveries were obtained when the nanoparticles were treated with 7 mol L^{−1} HNO_3 at ambient temperature for 20 min.

The restoration process was improved by heating in a boiling water bath, but in this case a partial dissolution of the MnFe_2O_4 was also observed.

For optimization of analyte recovery, the concentration of HNO_3 was varied at three levels (3, 5, 7 mol L^{−1}) and warm-up time was 15 or 20 min.

The obtained recoveries for all tested elements are shown in Fig. 7. According to their behaviour during elution, the tested elements could be divided into three groups. The influence of nitric acid concentration on recoveries of V, Cu and Pb is negligible. For Co and Zn the elution with 5 mol L^{−1} HNO_3 led to better recoveries, but 7 mol L^{−1} HNO_3 did not improve recoveries any further. Significantly influenced by the concentration of nitric acid were recoveries of Ni, As, Se, and Cd. For all of them, $R\%$ gradually increased with increasing concentration of acid. The most critical is the recovery in the final solution of As, Se and Cd.

Even when performing elution with 7 mol L^{−1} HNO_3 the obtained recoveries were unsatisfactory ($R_{\text{As}} = 82\%$; $R_{\text{Se}} = 54\%$; $R_{\text{Cd}} = 77\%$). For this reason the time for heating was extended up to 20 min (at highest acid concentration of 7 mol L^{−1}). As a

result, recoveries above 90% were obtained for all tested analytes with the exception of Se ($R = 75\%$).

In the final procedure the solid phase was treated with 0.5 mL of 7 mol L^{−1} HNO_3 in a water bath for 20 min and then the obtained solutions were additionally diluted up to 5 mL before ICP-MS analysis.

3.3.5. Comparison of MnFe_2O_4 with Fe_3O_4 NPs and other sorbents. The results from the optimisation of the SPE procedure for nine elements obtained with the new sorbent were compared to those obtained with the well-studied magnetite NPs.

To this end, the optimization of SPE was repeated using Fe_3O_4 NPs synthesized in our laboratory (Table 1). The results of the optimised MnFe_2O_4 NP SPE procedure were compared also with previous publications where magnetite NPs were used as sorbent or the separation procedure was based on complex reaction with APCD (Table 1).

The MnFe_2O_4 sorbent investigated in this work shows a capability for quantitative extraction of Me–APDC complexes in a broad range of pH values. In comparison, when the same experiment was done with Fe_3O_4 NPs a shorter pH interval (pH 4–8) was observed. This can be attributed to the higher solubility of magnetite in acidic media. Our results for the extraction degree of Me–APDC complexes are in agreement with the data obtained for SPE of Me–APDC complexes on sodium dodecylsulphate-coated alumina⁴³ and the pH range is higher than reported for other sorbents.^{17,34,36,42}

The mass of MnFe_2O_4 needed for extraction of nine metal ions is half of the corresponding values if using Fe_3O_4 (in our study and modified NPs in ref. 17). It should be noted that the quantity of manganese ferrite NPs in our study is at least one order of magnitude lower than that of other sorbents.^{34,36,42,43}

Concerning the pre-concentration ability, expressed as the ratio of volume of sample/eluent, the proposed magnetic NPs SPE is comparable to other published SPE procedures.^{36,42,43}

The only benefit of magnetite NPs is that the quantitative recoveries for all studied elements (with the exception of As,

Table 1 Comparison of new MnFe_2O_4 sorbent with Fe_3O_4 NPs and other sorbents

Sorbent	Analytes	pH range for $E\% > 95$	Mass of sorbent (mg)	Ligand mass (mg)/type	Sample/eluent volume (mL)	Eluent	Method	Ref.
MnFe_2O_4 NPs	V, Co, Ni, Cu, Cd, Pb, Zn, As, Se	3–9	5	60/APDC	50/5	0.5 mL ^a 7 mol L ^{−1} HNO_3	ICP-MS	This work
Fe_3O_4 NPs	V, Co, Ni, Cu, Cd, Pb, Zn, As, Se	4–8	10	60/APDC	50/5	0.5 mL ^a 5 mol L ^{−1} HNO_3	ICP-MS	This work
Fe_3O_4 NPs modified with decanoic acid	Cd, Co, Cr, Ni, Pb, Zn	10	12	MR ^b /PAN	50/0.3	0.3 mL 0.25 mol L ^{−1} HCl in propanol	ICP-OES	17
Sodium dodecylsulphate-coated alumina	Cu, Ni, Cd, Pb, Co, Fe	2–8	1500	100/APDC	20/3	3 mL 4 mol L ^{−1} HNO_3	ICP-MS	43
Multiwalled carbon nanotubes	Cu, Cd, Pb, Zn, Ni, Co	2–6	300	1/APDC	25–400/10	10 mL 1 mol L ^{−1} HNO_3 in acetone	FAAS	34
Amberlite XAD-4 resin modified	Cd, Cu, Mn, Ni, Pb, Zn	4–7	1000	Coated with APDC	100/10	10 mL 4 mol L ^{−1} HNO_3	ICP-OES	42
Nano-silver silica gel modified	Pb	7–8	300	Coated with APDC	50/5	5 mL 3 mol L ^{−1} HNO_3	FAAS	36

^a Diluted up to 5 mL prior ICP-MS determination. ^b MR – molar ratio (PAN/metal ions) = 3 is given.

where $R = 84\%$) were obtained by using a lower acid concentration (5 mol L^{-1}) and a shorter heating time (15 min) in comparison to the MnFe_2O_4 NPs. But as a consequence, completely dissolved Fe_3O_4 enhances matrix suppression in ICP-MS measurements.

However, compared to the elution reported by Ramesh *et al.*⁴² and Tuzen *et al.*³⁴ the current procedure for MnFe_2O_4 utilizes 20 times less volume and lower acid concentration in the final solution subjected to instrumental analysis.

The advantages of the proposed MnFe_2O_4 sorbent for SPE of hydrophobic APDC complexes of nine elements can be summarised as follows: fast and effective extraction in a broad range of pH using a very small amount of unmodified NPs.

3.4. Analytical figures of merit of MnFe_2O_4 NPs-SPE-ICP-MS combination

In order to estimate the reliability of the proposed MnFe_2O_4 NPs-SPE-ICP-MS method five multi-elemental standard solutions with gradually increasing concentrations ($1\text{--}100 \text{ } \mu\text{g L}^{-1}$ for V, Co, Ni, Cd, Pb and $10\text{--}1000 \text{ } \mu\text{g L}^{-1}$ for Zn, As, Se) of target analytes were subjected to the SPE procedure under the optimized conditions (Section 2.4). The parameters of obtained calibration equations with corresponding standard deviations of the slope and intercept are presented in Table 2. The good precision of the calibration slopes (RSD% within the range from 0.5% for Pb to 6.3% for Ni) together with the high values of the correlation coefficients (>0.999) proved that the developed SPE method based on magnetic NPs is reproducible and applicable for pre-concentration when the quantity of the analyte in the initial sample is below $5 \text{ } \mu\text{g}$ for V, Co, Ni, Cu and Pb and $50 \text{ } \mu\text{g}$ for As, Se and Zn.

The enrichment factors (EF in Table 2) are calculated as the ratio of slopes for both calibration curves – the ones obtained when standard solutions were subjected to the SPE procedure (SPE calibration) and when standards were prepared by spiking of aliquots in the procedural blank (matrix matched calibration). Given that the ratio of the original to final volume of samples is 10, obtained enrichment factors showed that the optimized SPE

Table 2 Characteristics of calibration curves obtained by magnetic (MnFe_2O_4) NPs-SPE-ICP-MS with enrichment factors (EF)

Element [isotope]	Parameters of the calibration equation ^{a,b}			EF
	Slope \pm SD	Intercept \pm SD	Correl. coeff.	
V [51]	1.14 ± 0.01	0.02 ± 0.04	0.9998	10
Co [59]	1.17 ± 0.05	1.8 ± 0.1	0.9997	10
Ni [60]	0.240 ± 0.015	0.42 ± 0.04	0.9991	10
Cu [65]	0.298 ± 0.005	0.19 ± 0.01	0.9999	10
Zn [66]	0.149 ± 0.001	0.87 ± 0.09	0.9997	9.9
As [75]	0.150 ± 0.005	0.01 ± 0.02	0.9995	9.1
Se [82]	0.0092 ± 0.0004	0.002 ± 0.003	0.9991	7.4
Cd [111]	0.435 ± 0.009	0.04 ± 0.05	0.9993	9.8
Pb [208]	1.122 ± 0.006	0.14 ± 0.03	0.9996	10

^a Five calibration standards were used with the following concentrations: 1, 5, 10, 50 and $100 \text{ } \mu\text{g L}^{-1}$ for V, Co, Ni, Cd, Pb and 10, 50, 100, 500 and $1000 \text{ } \mu\text{g L}^{-1}$ for Zn, As, Se. The concentration interval for calibration is $1.0\text{--}100 \text{ } \mu\text{g L}^{-1}$ for V, Co, Ni, Cd, Pb and $10\text{--}1000 \text{ } \mu\text{g L}^{-1}$ for Zn, As, Se.

^b Rh was used as internal standard.

procedure provides a quantitative extraction of all analytes except for As and Se.

As seen from Table 2, the intercept values for Co, Ni, Cu, Zn and Pb are high, which is an indication for detectable contamination in the blank sample. Taking into account that traces of these elements are declared by the manufacturer of the metal salts used for synthesis, this contamination is supposed to be inherent for the specified NPs and reproducible for the analytical procedure.

3.5. Application of the proposed magnetic NPs-SPE-ICP-MS procedure

The suggested procedure was validated by analysis of urine certified reference material SeronormTM 201205. It must be noted that for the used reference materials only the total element concentrations were certified. In their publication Yu *et al.*⁴⁴ emphasized that a variety of arsenic species are present in urine including arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine oxide (TMAO), arsenobetaine (AB), and arsenocholine (AC).

To investigate whether different arsenic species are extracted during the developed SPE procedure, additional experiments were carried out. First the retention of both inorganic forms As(III) and As(V) was examined using single-element standards. There was no difference in recoveries for different oxidation states of inorganic As. Moreover, the $R\%$ obtained using arsenic mono-elemental solutions was statistically indistinguishable from that when a multi-elemental standard was used.

In order to check whether the presence of organo-arsenic compounds could affect the correct determination of As in urine, two alternative sample treatments before SPE were compared. CRM was treated with HNO_3 and alternatively a more powerful oxidising mixture of $\text{HNO}_3 : \text{H}_2\text{O}_2 = 3 : 1$ was tested (see Section 2.5).

The selected calibration strategy capable of compensating for the matrix effect and partial recovery for As and Se was “SPE calibration” using Rh as internal standard for compensation of the instrumental drift.

The results obtained by magnetic NPs-SPE-ICP-MS with corresponding certified values and method detection limits are listed in Table 3. The MLOD were calculated using eqn (4).

$$\text{MLOD}_{\text{SPE}} = (3 \times \text{SD}_{\text{Bl}}/\text{Slope})/\text{EF} \quad (4)$$

where: MLOD is the method limit of detection; SD_{Bl} is the standard deviation of signals measured for 5 independent replicates of SPE blank solutions, prepared on different days; Slope is the slope of SPE calibration; EF is the corresponding enrichment factor.

The measured concentrations for Co, Ni, Cu, Zn, Cd and Pb are in good agreement with the certified values for both sample preparation approaches. Significantly lower (than certified) concentrations for As and Se when the sample was treated only with nitric acid could be attributed to the incomplete destruction of organo-metallic species.

The problem can be solved using a stronger oxidizing medium for sample pre-treatment. When urine was treated with $\text{HNO}_3 + \text{H}_2\text{O}_2$, the obtained sensitivities by SPE calibration were lower

Table 3 Validation of magnetic (MnFe₂O₄) NPs-SPE-ICP-MS by analysis of urine certified reference material Seronorm™ 201205

		Magnetic NPs-SPE–ICP-MS				ICP-MS analysis of urine by method of standard addition	
Element [isotope measured]	Assigned value ($\mu\text{g L}^{-1} \pm U$)	Treated with HNO ₃		Treated with HNO ₃ : H ₂ O ₂ (3 : 1)			
		Obtained value ^a ($\mu\text{g L}^{-1} \pm U^b$)	MLOD _{SPE} ^c ($\mu\text{g L}^{-1}$)	Obtained value ^a ($\mu\text{g L}^{-1} \pm U^b$)	MLOD _{SPE} ^c ($\mu\text{g L}^{-1}$)	Obtained value ($\mu\text{g L}^{-1} \pm U^b$)	MLOD _{StAdd} ^f ($\mu\text{g L}^{-1}$)
V [51]	25.2 ± 1.4	22 ± 1.8	0.01	25 ± 2.4	0.02	29 ^d ± 1.2	0.2
Co [59]	10.0 ± 0.6	11.1 ± 0.9	0.04	8 ± 1.8	0.1	10.6 ± 0.8	0.1
Ni [60]	50.4 ± 3.2	52.1 ± 2.6	0.05	51 ± 3.3	0.1	55 ± 2.2	0.2
Cu [65]	78 ± 8 ^e	70 ± 6	0.1	72 ± 7	0.3	77 ± 7	0.8
Zn [66]	1168 ± 92	1230 ± 30	0.7	1040 ± 33	1.5	1280 ± 40	2.3
As [75]	142 ± 6	34 ± 1.1	0.1	121 ± 16	0.3	174 ^d ± 15	2.2
Se [82]	58.6 ± 3.1	52 ± 3	0.2	59 ± 10	0.7	66 ± 9	3.4
Cd [111]	4.6 ± 0.4	5.1 ± 1	0.07	4.7 ± 2	0.15	5.4 ± 1	0.3
Pb [208]	40.3 ± 2.6	45 ± 4	0.08	44 ± 4	0.08	42 ± 2	0.6

^a Five replicate samples following the whole SPE procedure were analysed. ^b Expanded uncertainty is calculated using $k = 2$. ^c Cu content in Seronorm™ 201205 is given as analytical value with corresponding SD. ^d Measurements were performed with He as collision gas. ^e MLOD_{SPE} calculated according to eqn (4). ^f MLOD_{StAdd} calculated according to eqn (5).

than those for samples treated with HNO₃ only. The observed effect is probably due to the presence of incompletely destroyed hydrogen peroxide in the solution subjected to SPE. The sensitivity loss is reflected in a worsening of the detection limits with an average factor of 3.

Finally, if the determination of As and Se in urine samples is desirable, pre-treatment with HNO₃ : H₂O₂ is necessary, but it increases MLOD (see Table 3). For all other analytes lower detection limits without compromising the accuracy were obtained when only HNO₃ was used for urine sample pre-treatment.

The SPE procedure was also compared with the results from ICP-MS analysis of a diluted certified reference material. Here, all the measures to overcome the matrix effect mentioned in Section 3.2 were taken. Briefly V and As were measured in He mode, ⁶⁵Cu isotope free from polyatomic interference was chosen for analysis and the method of standard addition was used for calibration. The results from urine CRM analysis without preliminary separation are also given in Table 3. The statistically different values obtained for V and As indicate that even using collision gas (He) the spectral interferences cannot be eliminated and previous separation of target analytes from matrix is needed.

MLOD for urine analysis by the method of standard addition are calculated by eqn (5).

$$\text{MLOD}_{\text{StAdd}} = 3 \times \text{SD}_{\text{BI}} \times \text{DF}/\text{Slope} \quad (5)$$

where: MLOD is the method limit of detection; SD_{BI} is the standard deviation of signals in blank solution from MW acid digestion (5 replicates); DF is the dilution factor, Slope is obtained by the method of standard addition.

MLOD obtained with the developed magnetic NPs-SPE-ICP-MS method were improved by factors in the interval 3–20 in comparison to the ICP-MS analysis of urine by the method of standard addition.

One inherent drawback of the method of standard addition is the increase of the overall analysis time. In our case, because of the necessity to measure V and As in collision mode, the duration of ICP-MS measurement is additionally increased almost twice

(128 s) with respect to the time for measurement of solutions after SPE (86 s). Hence the instrumental measurement for analysis of 12 urine samples (including external calibration with 5 standards) developed by NPs-SPE-ICP-MS should take less than 30 min. This is at least three times less than the duration for analysis of the same number of samples in the case of using the method of standard addition. Taking into account the sample preparation step (MW treatment) the time for direct analysis of twelve urine samples by the method of standard addition as a whole is comparable with that for the magnetic (MnFe₂O₄) NPs-SPE-ICP-MS procedure for the same number of samples. This proves that the NPs-SPE-ICP-MS method is comparable in respect of sample throughput, but offers effective analyte separation from urine matrix and easier calibration, and shortens the ICP-MS measurement time.

In this study no special investigation was made for potential interference from concomitant matrix ions. Nevertheless, the good coincidence of the measured with certified values in such a highly salty matrix as urine is evidence that the proposed magnetic NPs-SPE-ICP-MS method is adequate in the presence of the following ions at levels certified by the manufacturer of Seronorm™: Cl (127 ± 4 mmol L⁻¹), K⁺ (1900 mg L⁻¹), Na⁺ (2300 mg L⁻¹), Ca²⁺ (110 mg L⁻¹), Mg²⁺ (70 mg L⁻¹), Rb²⁺ (1.17 mg L⁻¹) and Al, Ba, Be, Bi, Cr, Cs, Li, Mo, Sb, Sc, Sn, Sr, Te, Ti, Tl below 1 mg L⁻¹.

Table 4 Concentration of the elements in $\mu\text{g L}^{-1}$ with corresponding expanded uncertainty U ($k = 2$), obtained by magnetic NPs-SPE-ICP-MS analysis of a real urine sample, using MnFe₂O₄

Element [isotope measured]	Urine sample	Urine + spike		
	($\mu\text{g L}^{-1} \pm U$)	Added ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1} \pm U$)	Addition recovery (%)
V [51]	0.83 ± 0.09	10	10.6 ± 0.9	98
Co [59]	<0.3	10	9.9 ± 0.7	99
Ni [60]	24.4 ± 1.2	10	33.9 ± 1.6	95
Cu [65]	27.1 ± 1.3	10	36.6 ± 1.9	95
Zn [66]	963 ± 20	100	1060 ± 50	96
Cd [111]	5.4 ± 0.6	10	15.2 ± 1.2	98
Pb [208]	46.9 ± 1.6	10	57.2 ± 1.6	103

Table 5 Comparison between different separation techniques applied for element analysis in urine samples with proposed magnetic NPs-SPE-ICP-MS method

Separation method (mode of experiment)	Elements	Type of sorbent (mg)	EF	MLOD ($\mu\text{g L}^{-1}$)	Ref.
SPE-ICP-MS (batch)	Cd	Chelating resin NOBIAS P1	1	0.012 ^a	46
SPE-ICP-MS (on-line)	Mn, Co, Ni, Cu, Zn, Cd, Pb	PTEE sample loop	7–10	0.003–0.5	45
Magnetic NPs-SPE-ICP-MS (on-line)	Mn, Co, Cu, Zn, Pb	PAA-Fe ₃ O ₄ NPs	1	0.04–0.6	6
MnFe ₂ O ₄ NPs-SPE-ICP-MS (batch)	V, Co, Ni, Cu, Zn, As, Se, Cd, Pb	MnFe ₂ O ₄ NPs	10	0.01–0.7	This work

^a MLOQ has been reported.

The developed method was also applied for analysis of a human urine sample taken from a laboratory worker. Into a portion of the urine sample an aliquot of a multi-elemental standard (Merck VI) was added before SPE.

The measured concentrations into original and spiked samples of the element (in $\mu\text{g L}^{-1}$) with corresponding expanded uncertainty (U , at $k = 2$) are given in Table 4.

All measured concentrations (with the exception of Cd and Pb) in the human urine sample were lower than those in CRM analysed before. Because of this, for MW sample treatment only HNO₃ was preferred. In this case the concentrations of As and Se could not be measured accurately but the detection limits for all other elements are better. The obtained high recoveries of the spiked concentrations ($R > 95\%$) proved the reliability of the proposed magnetic NPs-SPE-ICP-MS procedure.

Finally the proposed MnFe₂O₄ NPs-SPE-ICP-MS procedure was compared with other published methods for analysis of essential and toxic elements in urine samples (Table 5).

The developed procedure for magnetically assisted SPE prior to ICP-MS analysis provides simultaneous determination of 9 elements and achieves comparable (or superior, with the exception of Co and Cd in ref. 45) detection limits. The obtained enrichment factor for urine analysis is also comparable to or better than that for SPE-ICP-MS methods proposed in the literature.

4. Conclusions

The unmodified MnFe₂O₄ NPs are a promising sorbent for SPE. Fine and stable NPs can be easily synthesized by co-precipitation of a stoichiometric mixture of metal ions with sodium hydroxide. The stronger magnetic properties of manganese ferrite NPs, in comparison to magnetite, accelerate their separation from the sample solution.

Higher stability of manganese ferrite in acidic media allows an increase of the working pH range and alleviates the matrix effect due to the dissolved NPs in the final solution.

Despite that the separation was made in batch mode, the overall SPE procedure is fast and simple. MnFe₂O₄ is a better alternative for SPE of APDC complexes of V, Co, Ni, Cu, Zn, As, Se, Cd and Pb than the commonly used Fe₃O₄.

The combined MnFe₂O₄ NPs-SPE-ICP-MS method proved to be effective for group determination of trace elements in urine.

The preliminary sample treatment with a mixture of HNO₃ + H₂O₂ was a prerequisite for accurate determination of As and Se, but at the expense of a worsening of MLOD. The MLOD were influenced by the blank sample, but nevertheless they were better than those for direct urine analysis.

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