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APPLICATION OF BARE AND SILICA-COATED $MnFe_2O_4$ MAGNETIC NANOPARTICLES AS A SORBENT FOR SOLID PHASE EXTRACTION AND ICP-OES TRACE ELEMENTS DETERMINATION

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ABSTRACT

Magnetic nanosized sorbent material based on $MnFe_2O_4$ (MnNPs) was synthesized by co-precipitation. Silica coated nanoparticles (SMnNPs) were obtained and both types coated and non-coated nanoparticles were tested for solid phase exstraction of V, Co, Cr, Ni, Cu, Zn, Pb and Cd complexes with ammonium pyrrolidine dithiocarbamate (APDC).

The analytes restoration into the final solution was achieved by treatment with 7 mol L^{-1} nitric acid at 25°C. The elution of elements for 10 min from both kinds of nanoparticles and complete digestion of the bare ones for 4h were compared with respect to the recovery and the level of matrix effects in ICP-OES.

The observed matrix suppression of emission signals in the range 12% (Cu) to 37% (Cd, Pb) was caused by the high acid concentration. Dilution of the final solution prior instrumental analysis to 2.8 mol L^{-1} nitric acid gives matrix effect reduction by a factor of 3 to 5, but also decreases the enrichment factor. There were no spectral interferences when SMnNPs eluates were measured. Due to the presence of Fe and Mn the obtained emission spectrum was significantly complicated in the case of bare MnNPs, hence special attention should be paid to the emission line selection and spectral interference corrections.

The elution of non-modified MnNPs was preferred instead of total digestion to reduce the matrix effects.

Using SMnNPs quantitative recoveries were obtained for Co, Cu and Ni, while for other elements R% were in range 60% – 85%. For all analytes R%≥90% were achieved with the exception of Cd (R=72%) applying bare MnNPs.

At the optimized SPE conditions an enrichment factor of 10 was obtained which allows detection limits decrease by factors 2–7 (SMnNPs) and 3–8 (MnNPs), in comparison to direct ICP-OES determination.

Key words: *magnetic nanoparticles, solid phase extraction, trace elements, ICP-OES*

INTRODUCTION

The utilization of nanoparticles in the solid phase extraction procedure for separation and pre-concentration of target analytes is a topic of growing interest[1–3]. The application of magnetic nanoparticles (MNPs) is promising because they combine the general advantage of active surface of nanosized materials having high area to volume ratio with superparamagnetic properties which allows easy separation from the sample solution by means of external magnet and can simplify the analytical procedure[1, 3, 4].

Among different nanoparticles with magnetic properties[5] only the surface modified magnetite (Fe_3O_4) have been exploited as a sorbent in the solid phase extraction procedures (SPE) for trace elements[6–15] and speciation[16–18] analysis.

The mechanisms for elements retention on the surface of nanoparticles could be summarized as follow: i) chemical bonding of the analytes with active groups linked to the surface [7–12, 14–18] or ii) sorption of the element complexes, preliminary formed in sample solution[6, 13]. To the best of our knowledge the sorption of the hydrophobic complexes on the surface of non-modified magnetic nanoparticles has not been studied yet.

Different approaches for surface modification of the sorbent could be distinguished. A modification with active ligands as: polyacrilic acid was used for group SPE of Mn, Co, Cu, Zn, and Pb[8]; 1-(2-pyridylazo)-2-naphthol (PAN) was used for SPE of Mn[9] and morin was used for Zn[10] and Cu[15].

Surfactants anchored chemically or physically adsorbed on the surface of nanoparticles may form single or double layer (hemimicelles, mixed hemimicelles, and admicelles) which stabilizes the solid phase in suspension and improves extraction efficiency[6, 13]. The modification of magnetic nanoparticles with decanoic acid and sodium dodecyl sulphate have been developed from Faraji et al.[6, 13] for SPE of Cd, Co, Cr, Ni, Pb, Zn as hydrophobic PAN complexes and mercury-Michler's thioketone complexes respectively.

Most of the methods incorporate two modification steps: preliminary covering of the nanoparticles with silica layer and further surface modification with complexing agent. The silica layer ensures sorbent protection in acidic media, decreases the agglomeration propensity but at the expense of loss of magnetic properties[1]. Silica coated nanoparticles additionally modified with γ-mercaptopropyltrimethoxysilane have been applied for fast and selective SPE of trace amounts of Cd, Cu, Hg, and Pb[12]; for speciation of inorganic Te[17] and for microextraction of Cd, Pb, and Hg from HepG2 cells[7]. The same group used the silica covered Bismuthiol-II – immobilized magnetite nanoparticles for SPE of trace amounts of Cr, Cu and Pb[14] and amino-modified silica-coated magnetic nanoparticles for speciation of inorganic As[18]. Wu et al. reported application of the silica-coated Fe_3O_4 nanoparticles modified with N-(2-aminoethyl)-3-aminopropyltrimethoxy-silane for speciation of Cr[16]. Magnetite nanoparticles modified with 3-(trimethoxysilyl)-1-propantiol and subsequent immobilized with 2-amino-5-mercapto-1,3,4-

thiadiazole have been employed for separation and preconcentration of trace amounts of Ag, Cd, Cu, and Zn[11].

In most of the published papers MNPs-SPE methods were combined with ICP-OES[6, 9–11, 13, 14] or ICP-MS[8, 12, 17, 18] as instrumental techniques for detection. However the study of non-spectral and spectral matrix effect in solutions obtained after SPE was not found.

Substituted iron oxides such as $CoFe_2O_4$[19] or $MnFe_2O_4$[20] have been recently applied for SPE of UV filters from cosmetic samples and bovine serum albumin (BSA) respectively. Hu et al[21] investigated the properties of substituted ferrites with common formula $MeFe_2O_4$ (where Me =Mn, Mg, Zn, Cu, Ni and Co) for removal of Cr(VI) from synthetic electroplating wastewater. The authors reported that among all tested sorbents $MnFe_2O_4$ nanoparticles have shown the strongest magnetic properties and the highest surface area which makes them promising for SPE. In our previous investigation[22] sorption of the hydrophobic complexes of V, Co, Ni, Cu, Zn, As, Se, Cd, Pb with ammonium pyrrolidine dithiocarbamate (APDC) on non-modified Fe_3O_4 and $MnFe_2O_4$ nanoparticles was studied. Optimized SPE method for group pre-concentration was applied for ICP-MS determination of target analytes in urine samples. Both types of evaluated MNPs were found to be effective as sorbents for Me-APDC complexes and final solutions were compatible with ICP-MS.

The aim of present study was to compare the applicability of bare and silica coated $MnFe_2O_4$ nanoparticles as sorbents for group SPE of V, Co, Cr, Ni, Cu, Zn, Pb and Cd by means of sorption of their APDC complexes preliminary formed into the sample solution combined with subsequent ICP-OES determination.

EXPERIMENTAL

Instrumentation

An inductively coupled plasma optical emission spectrometer ICP-OES Optima 4300 DV Perkin Elmer (Perkin Elmer Corporation, Shelton, CT) equipped with flow focusing nebulizer OneNeb® (Ingeniatrics S. L. Seville, Spain) was used in this study. The instrumental conditions are presented in Table 1.

For size characterization of studied MnNPs and SMnNPs a JEM-2010 high resolution transmission electron microscopy (HR-TEM) coupled to an

Inca Energy TEM100 energy dispersive X-ray spectrometer (EDS) from Oxford Instruments (Marlow, United Kingdom) was used.

Table 1. *The instrumental conditions of ICP-OES analysis*

Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.5 mL min^{-1}
Frequency of RF generator	40 MHz
RF generator power	1.55 kW
Observation mode	Axial
Nebulizer	OneNeb® (Ingeniatrics S. L. Seville, Spain)
Sample flow rate	0.5 mL min^{-1}
Element /Wavelength (nm)/	Cd(I)[a] 228.802 (R); Cd(II) 214.440; Cd(II) 226.502; Co(II) 228.616 (R); Co (II) 230.786; Cr(II) 267.716 (R); Cr(II) 205.560; Ni(II) 231.604 (R); Ni(II) 221.648; Ni(I) 232.003; Cu (I) 327.39 (R); Cu(II) 213.597; Pb(II) 220.353 (R); Pb (I) 217.000; V (II) 290.880 (R); Zn(II) 206.200 (R); Zn(I) 202.548

[a] in brackets: I is indication for atom emission line; II is indication for ion emission line R is recommended by the manufacturer analytical line.

An 800 Series Digital hot plate stirrer from VWR (Darmstadt, Germany) and an UP200S-Stand-Mounted ultrasonic processor from Dr. Hielscher (Teltow, Germany) with 200W effective power/amplitude output and working frequency of 24 kHz, and with a S7 titanium sonotrode (7mm diameter, 100mm length) were used for MNPs synthesis and surface modification. A micro pH 2002 pH-meter from Crison (Alella, Spain) was used for the pH measurements.

Reagent and samples

Sodium hydroxide and ammonium hydroxide solution (25% (w/v), d=0.91g mL^{-1}) reagent-grade used for nanoparticles synthesis and pH adjustment were purchased from Scharlau (Barcelona, Spain). Manganese dichloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) from VWR BDH Prolabo (UK) and iron trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$) from Sigma–Aldrich (Steinheim, Germany) were used as a precursor salt for synthesis. Tetraethyl orthosilicate (TEOS) Sigma–Aldrich, ethanol and acetic acid LC-grade from Scharlau were used for nanoparticles surface modification.

The complexing agent – ammonium pyrrolidine dithiocarbamate (APDC), (Sigma Aldrich) was added as 2% solution in water (daily prepared). ICP multi-element standard solution IV Merck (Darmstadt, Germany) and single element solutions of V 1000 mg L^{-1} High Purity Standards (Charleston, UK) after appropriate dilution were used to prepare a model solution for SPE procedure optimization as well as for the preparation of calibration standards.

Ultra-pure water (resistivity ≥18MΩcm) obtained by a NANOpure II system from Barnstead (Boston, MA, USA) was used for the preparation of all solutions.

Magnetic nanoparticles synthesis and surface modification

Magnetic nanoparticles were synthesized by co-precipitation of solution containing Mn^{2+} and Fe^{3+} ions in basic media. Before the synthesis, the precursor solution (V=500 mL) with concentrations of metal ions 0.017 mol L^{-1} for Mn^{2+} and 0.033 mol L^{-1} Fe^{3+} (molar ratio Mn^{2+}: Fe^{3+} = 1:2) was heated to 30^0C and then 0.25 mol L^{-1} NaOH was added at once until pH~11 was reached. The produced suspension was additionally stirred keeping the temperature ~ 80^0C for 3 hours.

The magnetic nanoparticles were separated from a supernatant solution by means of external magnet and washed with double distilled water until pH=7 was reached then once more with ethanol. Nanoparticles were stored as suspensions in 50 mL double distilled water and were stable up to 6 months.

A part of the produced MnNPs was subjected to the surface modification following the procedure described for $CoFe_2O_4$ nanoparticles[19]. Briefly, separated and washed MnNPs were dispersed in 450 mL of ethanol using the ultrasound processor (the pulse and the amplitude was set for all the synthesis process at 100% and 80%, respectively). The solution was purget with argon to remove dissolved oxygen. Chilled (for 10 min at – 18° C) solution of 10.5 mL of ammonia in 140 mL of ultrapure water was added to the suspension. The mixture was sonicated for 15 min, and then chilled TEOS solution (22.5 g in 75 mL ethanol) was added near to the sonotrode with a pipette. After 60 min, the argon flow and the ultrasound energy were stopped and the particles were separated by means of external magnet.

Magnetic nanoparticles based SPE procedure

Solid phase extraction procedure was performed in a batch mode presented on Fig. 1. Parameters of procedure such as solution pH, sorbent and ligand amounts as well as time for separation were previously optimized[22]. Approximately 10 mg of the nanoparticles were transferred into a conical test tube (V = 50 mL). Model solutions and 25 mg APDC (as a 2% m/v solution) were added and then pH was adjusted at five. The extraction of metal chelates was performed by continuous shaking for 5 min. Magnetic nanoparticles with the adsorbed metal complexes were separated by means of permanent magnet for 5 min and then the supernatant solution was completely decanted. The separated solid phase was washed with 10 mL ultra-pure water.

For the analyte restoration in final solution 7 mol L^{-1} nitric acid was used at ambient temperature. Two approaches were tested: i) elution with 2 mL acid for 10 min for both types of nanoparticles (in this case non modified MnNPs were partially dissolved) and ii) prolonged treatment for 4 hours (for bare MnNPs only), that led to complete dissolution of solid phase.

The three different final solutions namely eluates obtained from SMnNPs and MnNPs and completely dissolved MnNPs were diluted with ultrapure water to final volume 5 mL and subjected to ICP – OES analysis.

ICP-OES determination of solutions obtained after SPE

The plasma axial observation mode was used for detection of analyte emission lines. The concentration of analytes into the final solutions obtained after SPE was calculated using matrix match calibration approach, where the calibrations standards (in interval 0–1mg L^{-1}) were prepared by addition of spikes from multi-element aqua standards into the procedural blank.

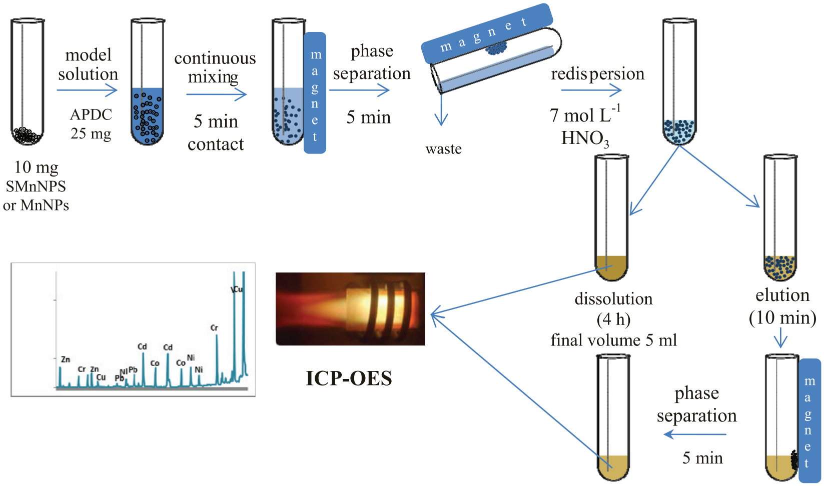

Figure 1. *Principal scheme of the magnetic nanoparticles based solid phase extraction procedure.*

RESULTS AND DISCUSSION

Magnetic nanoparticles characterization

Both synthesized magnetic nanoparticles (bare and silica coated) were characterized by TEM (Fig. 2A, B). Two fractions with mean diameters ~2 nm and ~20 nm could be distinguished for bare particles (Fig. 2C). The modification by silica layer led to the increased size and the finest fraction cannot be distinguished. Probably the smallest particles are agglomerated during the modification, but the mean size of the silica-coated manganoferrite nanoparticles is still below 50 nm. Finally it was proven by EDS analysis that manganoferrite particles were with desired molar ratio Mn:Fe = 1:2 which corresponds to the formula $MnFe_2O_4$

Optimization of ICP-OES determination

Three different final solutions obtained after SPE were subjected to ICP-OES analysis, namely final solutions obtained after SPE and: i) elution of analytes from SMnNPS, ii) elution of analytes from MnNPS for 10 min and iii) complete dissolution of solid phase (for MnNPS) for 4h. The matrix effects (spectral and non-spectral) were examined in all mentioned cases and correction approaches were proposed.

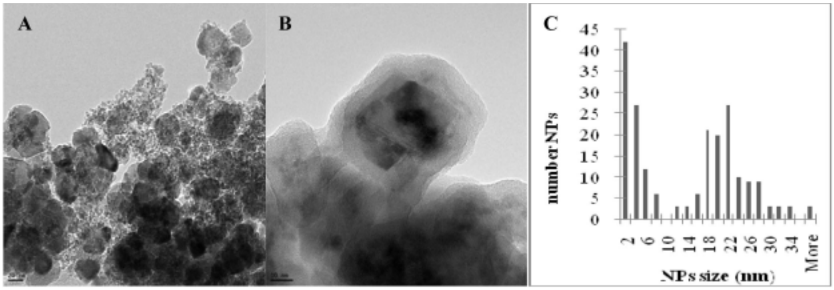

Figure 2. *TEM images of MnNPs (A) and SMnNPs (B) with size distribution diagram for* $MnFe_2O_4$ *NPs.(C)*

For estimation of the non-spectral matrix effect (Eq.1) sensitivities of analytes obtained in every sample fraction were compared to the common external calibration using aqua standard solutions containing only 1% (v/v) HNO_3 (0.14 mol L^{-1}) needed for stabilization.

$$MatrixEffect\ \% = \frac{Sens_{Matrix} - Sens_{AquaStd}}{Sens_{AquaStd}} \times 100 \qquad (1)$$

where: $Sens_{Matrix}$ is the slope of calibration line in the presence of studied matrix; $Sens_{AquaStd}$ is the slope of calibration line obtained using aqua standards containing 0.14 mol L^{-1} HNO_3.

Both borderline cases without dissolved solid phase (SMnNPs eluted with 7 mol L^{-1} HNO_3) and with completely dissolved solid phase (4h treatment of MnNPs) were compared. (Fig. 3) For all monitored emission lines the non-spectral matrix effect was comparable when eluats from SMnNPs and completely dissolved MnNPs were directly measured. Observed matrix suppression was within the interval 12% (Cu) to 37% (Cd, Pb) and it was caused mainly by the high acid concentration. Further dilution up to 2.8 mol L^{-1} led to the reduction of matrix effect by factor 3–5, but enrichment factors were lowered in this case. All further measurements were performed after dilution of the final solution prior instrumental analysis up to 5 mL. Even in this case matrix suppression up to 15% for Cd, Cr and Ni was detected. In order to solve the problem with matrix effects we choose to work with calibration standards prepared in procedural blank (Matrix matched calibration).

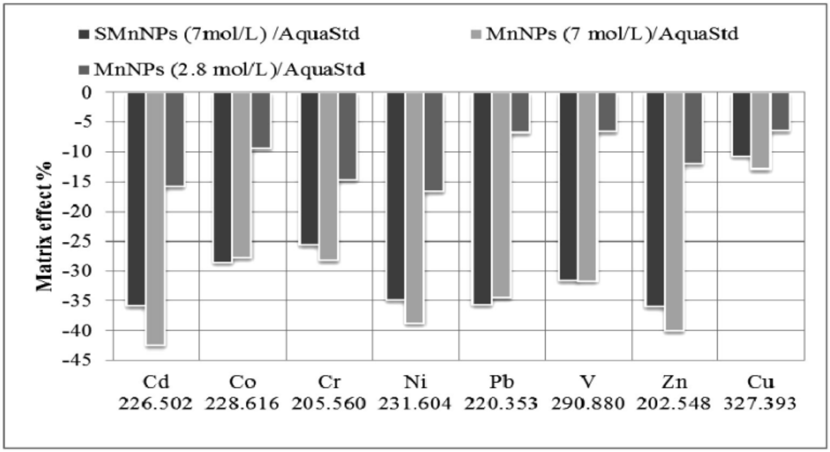

Figure 3. *Non spectral matrix effect on the analytes sensitivity in solutions after SPE procedure, compared to external calibration using aqueous standards.*

Spectral matrix effect was not observed when SMnNPs were used as a sorbent. Completely different behavior was detected in the case of non-modified MnNPs because of the presence of matrix elements (Fe and Mn) in the final solution. Elevation of the background signal was recorded in the both cases when non modified MnNPs were used for SPE (Fig. 4).

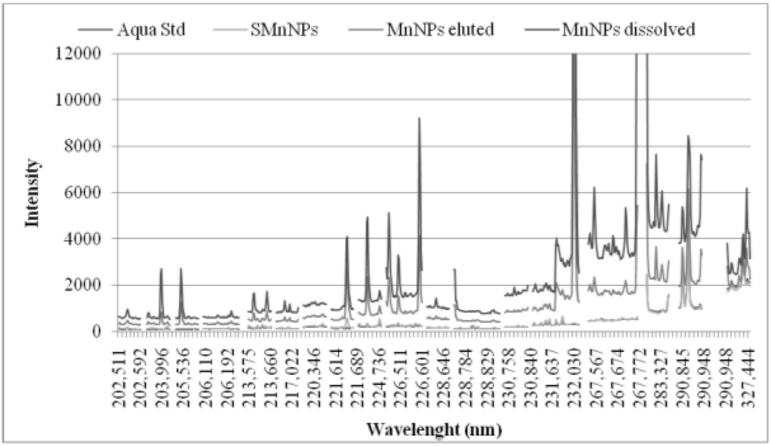

Figure 4. *Emission signals of the analytes in blank solutions obtained after SPE using three approaches for analytes restoration: elution from SMnNPs, MnNPs and dissolution of MnNPs.*

The mean enhancement of background (in comparison to aqua standard) was by factor of 3 for eluted MnNPs, and by factor of 6 when solid phase was completely dissolved. Probably this behavior is due to the band emission spectra of molecules or radicals formed by matrix components (i.e. Fe and Mn) in cooler regions of the plasma tail. As could be seen from figure 4 the obtained emission spectrum was significantly complicated due to the presence of Fe and Mn especially in the case of bare MnNPs. With increasing the concentration of matrix components even less sensitive emission lines of Fe and Mn could be detected.

For estimation of the spectral interferences at least two emission lines per analyte were monitored. Free from spectral interferences were the emission lines of Co 228.616 nm; Pb 220.353 nm; Zn 202.548 nm and V 290.880 nm. Spectral lines caused by matrix elements were observed near to the emission lines of Cd 214.440 nm and 226.502 nm; Cr 205.560 nm; Cu 327.390 nm and 213.597 nm; Ni 232.003 nm (Fig. 5).

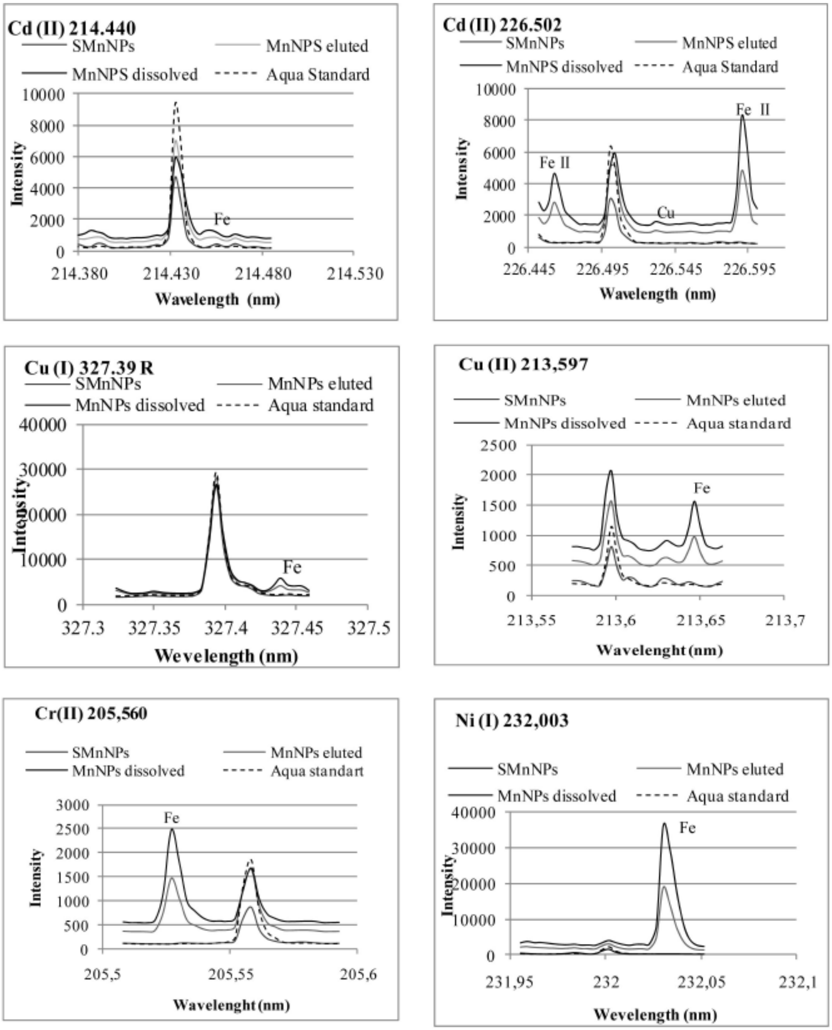

Figure 5. *The emission lines for analytes measured in solutions after SPE with SMnNPs and MnNPs compared to the corresponding aqua standard. Concentration of the elements in all solutions is 0.5 mg* L^{-1}

Nevertheless these lines could be used for analysis. To avoid any overlap of adjacent peaks of the analyte and interfering component it is recommended to measure the intensity at the analyte peak maximum, instead of the spectral peak area. The recommended by the instrument manufacturer emission line Cr 267.716 nm was overlapped by Mn 267.725 nm. The similar case was found for the line of Pb 217.000 nm interfered by Fe 216.995 nm. The last two lines are not suitable for analysis in the presence of manganoferrite matrix (Fig. 6).

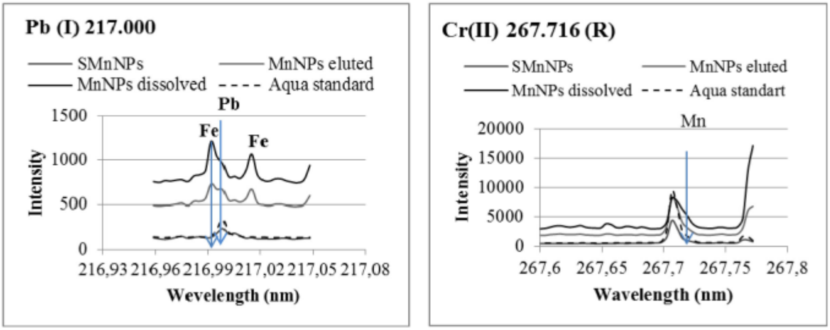

Figure 6. *The emission lines of analytes directly overlapped by the matrix components in solutions after SPE with SMnNPs and MnNPs compared to the corresponding aqua standard. Concentration of the elements in all solutions is 0.5 mg L* $^{-1}$

Analytical figures of merit

The recoveries (Table 2) obtained for model solutions of target analytes subjected to SPE-ICP-OES were calculated by equation (2).

$$R\% = \frac{Q_{SPE}}{Q_{initial}} \times 100 \qquad (2)$$

where: R% – recovery; $Q_{initial}$ is the initial analyte quantity in the model solution; Q_{SPE} – is the analyte quantity, measured after SPE procedure

When the MnNPS were used for SPE (for both restoration protocols) recoveries above 90% were observed for all tested elements with exception of Cd (R% = 78), while in the case of SMnNPs the recoveries above 90% were obtained only for Co, Cu, Ni and Pb, which proves that the surface of bare manganoferrite particles shows better adsorption properties towards Me-APDC complexes than siliconated ones.

For assessment of the method limits of detection MLOD (Table 3) in SPE the signals corresponding to 3 times standard deviation of blank solution were calculated as concentrations, using the calibration equations obtained by the method of matrix-matched calibration (standards prepared in procedural blank). Obtained values were lowered by the achieved pre-concentration factor. With the proposed SPE-ICP-OES procedure detection limits were decreased by factors in the range 2–7 (SMnNPs) and 3–8 for MnNPs. In respect to the MLOD the siliconated SMnNPs give better result, which is mainly due to the less pronounced matrix effect, but in this case incomplete recovery must be corrected by adequate calibration procedure. While for bare manganoferritte NPs, the sorption process is not problematic, but elution protocol should be kept as soft as possible in order to decrease the spectral interferences inherent for the matrix reach with Fe and Mn.

Table 2. *Recoveries (R%) of the studied elements, with corresponding standard deviations (n=5), obtained for both types of MNPs and different restoration protocols.*

R%±SD	**Cd 214.440**	**Co 230.786**	**Cr 205.560**	**Cu 327.393**	**Ni 231.604**	**Pb 220.353**	**V 290.880**	**Zn 202.548**
SMnNPs	**72 ± 3**	**92 ± 4**	**60 ± 2**	**93 ± 4**	**95 ± 4**	**93 ± 3**	**71 ± 2**	**69 ± 3**
MnNPs Eluted	**78 ± 2**	**97 ± 4**	**93 ± 3**	**91 ± 3**	**99 ± 3**	**100 ± 2**	**100 ± 1**	**91 ± 3**
MnNPs Dissolved	**78 ± 1**	**97 ± 3**	**97 ± 2**	**90 ± 3**	**98 ± 2**	**99 ± 1**	**99 ± 2**	**90 ± 2**

Table 3. *Method limits of detection (MLOD) in µg L^{-1} obtained by SPE procedure using bare and silica coated MnNPs compared to the instrumental limits of detection in aqua standards.*

	Cd 214.440	**Co 230.786**	**Cr 205.560**	**Cu 327.393**	**Ni 231.604**	**Pb 220.353**	**V 290.880**	**Zn 202.548**
Aqua standards	**0.35**	**0.89**	**1.71**	**0.67**	**0.74**	**6.97**	**7.73**	**0.80**
SMnNPs	**0.19**	**0.16**	**0.36**	**0.25**	**0.29**	**0.97**	**1.43**	**0.23**
MnNPs Eluted	**0.18**	**0.33**	**0.46**	**0.27**	**0.29**	**1.15**	**0.95**	**0.25**
MnNPs dissolved	**1.77**	**0.39**	**0.41**	**0.24**	**0.64**	**2.78**	**1.32**	**0.42**

CONCLUSIONS

SPE with bare and silica covered $MnFe_2O_4$ magnetic nanoparticles proved to be effective for the group pre-concentration of APDC complexes of V, Co, Cr, Ni, Cu, Zn, Cd and Pb. Silica modified $MnFe_2O_4$ NPs applied as a sorbent allows free from spectral interferences ICP-OES analysis, but with lower recoveries. Bare MnNPs are more effective sorbent for Me-APDC complexes, but the dissolved matrix during elution, causes a number of spectral interferences in ICP-OES. Hence, keeping the soft conditions during elution of analytes is strongly recommended in order to reduce the matrix effect. For analytical data handling, the maximum of spectral peak is suggested as more appropriate.

The optimized SPE method combines a simple synthesis, small amount of sorbent phase (10 mg), easy performance and good compatibility with ICP-OES.

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