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# Magnetic assisted solid phase extraction of trace elements by APDC impregnated silica coated manganese-ferrite nanoparticles

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Magnetic nanoparticles (MNPs) are widely used as solid phase extraction (SPE) sorbents. In present work the sorption efficiency of manganese-ferrite nanoparticles synthesized by two methods (co-precipitation and solution combustion) were compared. The investigated nanoparticles have a different size distribution i) mono-modal with average size ~13 nm for MNPs synthesized by solution combustion and ii) bi-modal for NPs produced by co-precipitation with sizes 2 nm and 25 nm. These physical parameters presume a difference in surface area which could reflect on effectiveness of SPE.

The application of MNPs for the purpose of elemental analysis often requires improvement of selectivity and stability in an acid media. Two steps modification of magnetic core, which includes: i) covering with silica in order to prevent its dissolution in acidic media and ii) impregnation with complexing agent – ammonium pyrrolidine dithiocarbamate (APDC) for selectivity improvement is proposed.

Modified manganese-ferrite magnetic nanoparticles ($MnFe_2O_4@SiO_2$-APDC NPs) were tested as a sorbent for solid phase extraction of Co, Cu, Zn, Mo, Cd, Tl, Pb and Bi prior their determination by ICP-MS. The experimental conditions influencing on sorption efficiency of tested elements on the $MnFe_2O_4@SiO_2$-APDC NPs surface as pH of solution and mass of sorbent were optimized. A selectivity of the extraction system can be improved by variation of the media acidity. For group solid phase extraction of all tested elements, the following compromise conditions were selected: pH = 5; 30 mg NPs; elution with 1 mol $L^{-1}$ $HNO_3$ at elevated temperature for 15 minutes.

It has been proven that solid phase extraction of Co, Cu, Zn, Mo, Cd, Tl, Pb and Bi on $MnFe_2O_4@SiO_2$-APDC NPs is reproducible and applicable for analysis by ICP-MS.

***Keywords**: magnetic nanoparticles, solid phase extraction, APDC modification*

## INTRODUCTION

Iron oxides (magnetite and hematite) or mixed ferrites with general formula $MFe_2O_4$ (where M = Mn, Co, Ni, Zn, etc.) are the most often used magnetic nanoparticles for SPE [1]. Undisputable advantages of these materials for dispersive SPE are their large contact surface, possibility for modification and easy separation of the sorbent by external magnetic field.

Various synthetic methods for preparing nanoparticles of mixed ferrites are described in the scientific literature. Among them the co-precipitation from $Mn^{2+}/Fe^{3+}$ aqueous solutions by adding a base under an inert atmosphere at room (or elevated) temperature is one of most often used method, because it is fast and easy for implementation. The size, shape and composition of magnetic nanoparticles depend on the type of salts used, ratio of $Mn^{2+}/Fe^{3+}$, temperature, pH and ionic strength of the solution [2]. This method offers high yields, but poor size control, and therefore the resulting NPs have a relatively broad size distribution.

Another well-known approach to obtaining nanomaterials is a solution combustion synthesis (SCS) [3-5]. It is based on self-sustained redox exothermic reactions between hydrated metal nitrates and fuel(s). Hydrated metal nitrates are typically used as oxidizer precursors, while the fuels represent a broad range of compounds including urea, glycine, citric acid, etc. The combustion reaction usually is initiated by preheating until a self-sustaining exothermic reaction arises, generating heat and releasing combustion gases. This leads to self-ignition, and in the certain parts of system, local temperatures reach from 500 to 3000 °C, depending on the combination of metal salts and fuel [5].

In most cases, a modification of NPs surface is necessary, when they are intended to SPE of elements. The construction of a surface protective layer of NPs is accomplished by using various inorganic components (such as silica or carbon), organic molecules, surfactants or polymers. Silica

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coating is most often used because of its acidic stability and thermal resistance [6, 7]. Modifications to improve selectivity are related to incorporation of functional groups on the NPs surface. For this purpose, S and N containing organic substances are preferred because of their ability to form stable complexes with various transition metals such as Cd, Cu, Hg, Pb, Ag, Zn, Cr, etc. [8].

Ammonium pyrrolidine dithiocarbamate (APDC) is a complexing agent, well-known in analytical practice, that acts as bidentate ligand and forms hydrophobic chelate complexes with more than 40 elements [9]. The metal-APDC complexes are stable over a wide pH range (2 ÷ 14), making this regent suitable for developing variety of separation - concentration methods such as co-precipitation [9, 10] liquid-liquid [11, 12], solid phase [13, 14] or cloud point [15, 16] extraction. The established methods are successfully combined with atomic spectroscopy techniques as: ICP-MS [9], ICP-OES [10], FAAS [12, 14, 15].

Different nano-sized sorbents such as carbon nanotubes [17] and unmodified magnetite and manganese-ferrite nanoparticles [18, 19] are used for sorption of Me-APDC chelates preliminary formed in sample solution. Recently Meng *et al* [20] proposed silica coated magnetite nanoparticles modified with APDC for SPE of Cu and Ni prior their FAAS determination. Despite APDC modification procedure, authors reported insufficient recovery of both analytes, without further addition of ligand to the extraction system.

In present investigation comparative study of two steps modification procedure and extraction abilities of $MnFe_2O_4$ NPs synthesized by different methods is proposed. An indirect experimental approach was used to evaluate the effectiveness of building a protective layer ($MnFe_2O_4@SiO_2$) over magnetic core in conducting a modification of magnetic nanoparticles prepared by co-precipitation and solution combustion methods. Protected nanoparticles are impregnated with a second layer of APDC, which facilitates the retention of metal ions by complexing reaction on the surface itself. The resulting $MnFe_2O_4@SiO_2$-APDC nanoparticles were applied for group solid phase extraction of Co, Cu, Zn, Mo, Cd, Tl, Pb and Bi prior to ICP-MS determination.

## EXPERIMENTAL

### *Instrumentation*

Quadruple Inductive Coupled Plasma Mass Spectrometer ICP-MS Agilent 7700 (Tokyo, Japan) with octopole reaction system (ORS) and helium as collision gas was used for SPE optimization and for final studies as well. Thirteen isotopes: $^{59}$Co, $^{63,65}$Cu, $^{66,68}$Zn, $^{95}$Mo, $^{111,114}$Cd, $^{205}$Tl, $^{206,208}$Pb, $^{209}$Bi and $^{103}$Rh (as internal standard) were monitored at 1 point per mass peak with 100 ms integration time with five replicates for each measurement.

ICP-OES - iCAP 6300 Duo Thermo (Thermo Fisher Scientific Inc.) with axial and radial plasma observation, equipped with a CID detector was used for estimation of silica modification efficiency. For this purpose, two emission lines of iron (Fe II 259.940 nm and Fe II 259.837 nm) were monitored.

High Resolution Transmitting Electron Microscope (HR-TEM) JEOL JEM-2010 equipped with an energy dispersion micro-analysis system (EDS) Inca Energy TEM100 Oxford Instruments (Marlow, United Kingdom) working with accelerating voltage 200 kV and resolution up to 0.20 nm was used for size characterization of studied $MnFe_2O_4$ NPs

Ultrasonic system with a UP 100H ultrasonic processor (Dr. Hielscher GmbH, Teltow, Germany) with a 24 kHz operating frequency and a maximum output of 100 W, equipped with a S7 titanium sonotrode (7 mm diameter, 100 mm long) was used in silica coating of magnetic NPs.

A permanent Fe-Nd-B magnet S-45-30-N (45 mm diameter and 30 mm height) from Supermagnete (Uster, Switzerland) was used to separate the solid phase from the solution during SPE experiments.

### *Reagents and standard solutions*

The precursors used for the synthesis of magnetic nanoparticles by the precipitation method - iron trichloride hexahydrate ($FeCl_3x6H_2O$), manganese dichloride tetrahydrate ($MnCl_2x4H_2O$) were purchased from Sigma-Aldrich Company Milwaukee, WI, USA and NaOH p.a (HIMTEKS LTD -Dimitrovgrad). Ammonia solution $NH_4OH$ (25% p.a., d = 0.91 g cm$^{-3}$ RAY-HIM product EOOD) and; $HNO_3$ (65% p.a., d = 1.40 g cm$^{-3}$ Merck Darmstadt, Germany) were used for pH adjustment. Ammonium pyrrolidine dithiocarbamate (APDC), (Sigma Aldrich); Tetraoethoxysilane (TEOS, Sigma-Aldrich) and ethanol (RAY-HIM product EOOD) were used in surface modification of nanoparticles.

A multi-element standard solution ICP: MU28: N; 100 mg L$^{-1}$ (CPA Chem, Stara Zagora Bulgaria) was used for preparation of model solutions and calibrators, after appropriate dilution. The final concentration of all elements in model solutions for SPE optimization was 10 µg L$^{-1}$. A standard solution of Rh - 100 mg L$^{-1}$ (CPA Chem, Stara Zagora Bulgaria) was used in all studies as internal standard for correction for instrumental drift and non-spectral matrix effect.

The surface water reference material SPS-SW1 - Level 1 (Spectrapure Standards as, Oslo, Norway) was used for validation of SPE procedure

### *Synthesis and modification of mangano-ferrite nanoparticles*

The co-precipitation method was described elsewhere [19]. Briefly, as the precursor solution mixture containing metal ions of $Mn^{2+}$ and $Fe^{3+}$ in a molar ratio of 1: 2 at a total molar concentration of both ions 0.05 mol $L^{-1}$, was used. To 500 mL of pre-heated (50° C) precursor solution, was added 100 ml of 0.25 mol $L^{-1}$ NaOH. The reaction mixture was heated up to 80 °C for 3 hours with continuous homogenization. The resulting nanoparticles were separated by a magnet and washed repeatedly with double distilled water (BDW) until pH = 7 of washed solution was reached, then once with ethyl alcohol. The nanoparticles are stored as slurry in BDW.

The magnetic nanoparticles synthesized by solution combustion method with which the study was conducted were obtained according to the procedure described in [5]. For synthesis, $Mn(NO_3)_2.4H_2O$ (Sigma Aldrich), $Fe(NO_3)_3.9H_2O$ (Sigma Aldrich) and glycerol as a reducing agent and subsequent thermal treatment at 400 °C for 2 hours were used.

### *Modification of nanoparticles.Modification of $MnFe_2O_4$ nanoparticles with $SiO_2$*

The core-shell type surface modification with the protective $SiO_2$ layer by was made by the Ströber method, by hydrolysis of TEOS in a basic medium and ultrasonic (US) treatment. To 5 g of manganese-ferrite nanoparticles, 450 ml of ethyl alcohol was added and the suspension is sonicated for ~ 30 min. To the ethanol suspension was added 140 ml of an ammonia solution (1 mol $L^{-1}$) cooled (for 10 minutes at -18 °C), and the US treatment is continued for 15 min. As a next step, 125 ml of a cooled solution of TEOS in ethyl alcohol (42.2% m $m^{-1}$) was added dropwise and US treatment continued for 1 hour. The modified nanoparticles are separated by a magnet and washed with BDW and ethyl alcohol.

### *Impregnation of silica-coated nanoparticles $MnFe_2O_4@SiO_2@APDC$*

Silica-coated nanoparticles were treated twice with 3 ml of 1 mol $L^{-1}$ $HNO_3$ in boiling water bath for 45 min in order to remove unmodified fraction before modification.

For impregnation ~ 0.1 g of $MnFe_2O_4@SiO_2$ nanoparticles are suspended in 20 ml of BDW, the pH of the solution is adjusted to pH = 3 (by adding 1 mol $L^{-1}$ $HNO_3$ or $NH_4OH$) and the suspension is homogenized for 10 min on shredder. Impregnation procedure was performed with 20 ml of APDC solution (2% m/v) for 2 hours at continuous stirring. The resulting $MnFe_2O_4@SiO_2@APDC$ nanoparticles are washed twice with BDW.

### *Procedure of solid phase extraction*

The extraction is carried out by adding of 30 mg nanoparticles to 50 ml model solution of the elements and the pH is brought to the desired value. The extraction was carried out by shaking for 30 min. A solid phase is separated by a magnet for 5 minutes. The supernatant solution was then poured out and solid phase was washed with BDW. Elution of elements is performed with 3 ml of 1 mol $L^{-1}$ $HNO_3$ by heating in a boiling water bath for 15 min. After removing of MNPs (by a magnet), the concentration of the target elements was determined by ICP-MS.

## RESULTS AND DISCUSSION

### *Characterization of magnetic nanoparticles*

The shape and size of the obtained nanomaterials is characterized by a transmission electron microscope (TEM) (Fig.1). From the images depicted, it is obvious that nanoparticles with approximately spherical shape were obtained in both synthetic procedures but by the SCS (Figure 1A), the MNPs have a narrower size distribution (mean size 13 nm), whereas in co-precipitation method (Figure 1B) the size distribution is bimodal, with two major fractions with diameters of ~2 nm and ~20 nm respectively. This implies different behaviour of the materials in both surface modification and their use as sorbents in SPE.

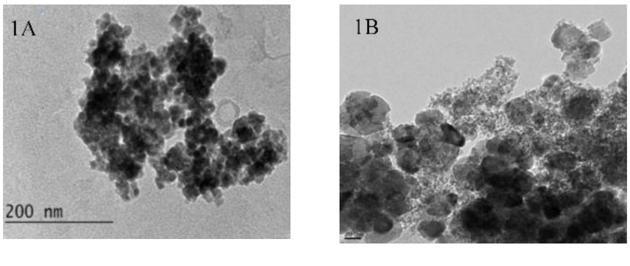

**Fig. 1.** TEM images of MnFe2O4 NPs synthesized by SCS (A) and co-precipitation (B)

### *Determining the efficiency of modification with $SiO_2$ shell on the magnetic core*

The difference in size (surface) of MNPs obtained by both synthetic procedures assumes that a different amount of TEOS will be needed for effective covering of magnetic core with silica layer. The quantity of TEOS was varied at two levels 4.5 g and 9 g per gram $MnFe_2O_4$ NPs. The efficiency of the core-shell modification was indirectly evaluated by treating the resulting $MnFe_2O_4@SiO_2$ nanoparticles with nitric acid (1 mol $L^{-1}$) at elevated temperature for 15 minutes. The concentration of dissolved Fe was determined by ICP-OES and the obtained results are summarized in Table 1.

**Table 1**. Amount of dissolved Fe (expressed as mg Fe per g of $MnFe_2O_4@SiO_2$ NPs) at different amounts of TEOS used for silica layer formation

| Type of nanoparticles | Quantity TEOS g for modification of 1g $MnFe_2O_4$ | mg Fe dissolved per1g $MnFe_2O_4@SiO_2$ |
|---|---|---|
| $MnFe_2O_4@SiO_2$ – co-precipitation | 4.5 | 0.85 |
| $MnFe_2O_4@SiO_2$ – SCS | 4.5 | 9.84 |
| $MnFe_2O_4@SiO_2$ – SCS | 9 | 3.86 |

As can be seen from the presented results 4.5 g of TEOS are sufficient to form the $SiO_2$ protective layer on $MnFe_2O_4$ nanoparticles synthesized by the co-precipitation method. When NPs produced by SCS are modified with the same amount of TEOS, the dissolved Fe is almost 11 times higher, which is an indication for ineffective formation of a protective shell over magnetic core, probably due to a larger surface area. Double amount of TEOS leads to decreasing of the dissolved Fe by a factor of ~3. Unfortunately, this still is higher than results for NPs obtained by co-precipitation, i.e. unprotected fraction remains after the procedure. In order to remove the unmodified MNPs before impregnation, we propose a preliminary treatment of the material synthesized by SCS with 1 mol $L^{-1}$ HNO3 at elevated temperature for 45 min. After "washing" step, the residual amount of Fe was decreased to 1.2 mg per 1g of NPs, which is comparable to the one for MNPs obtained by co-precipitation.

### *The impregnation process with ammonium pyrrolidine dithiocarbamate (APDC)*

The acidity of medium greatly impacts the efficiency of $MnFe_2O_4@SiO_2$ modification with APDC. On the one hand, the surface charge of the siliconized nanoparticles depends on pH – it is a positive at pH <3, zero at pH ~3 and negative at higher pH of solution. Surface charge determines the possibility of ligand retention on the nanoparticles. On the other hand, the speciation of ligand also directly depends on the pH ($pK_a$ (HPDC) = 3.300 ± 0.002). Preliminary studies on the effect of pH on impregnation efficiency have shown that the best results are obtained in an acid medium (pH ~2-3). Under these conditions, the surface charge of $MnFe_2O_4@SiO_2$ is ~ 0 or slightly positive, and the ligand presents in a predominant neutral form of pyrrolidine dithiocarbamic acid, which imply its physical adsorption on the MNPs surface.

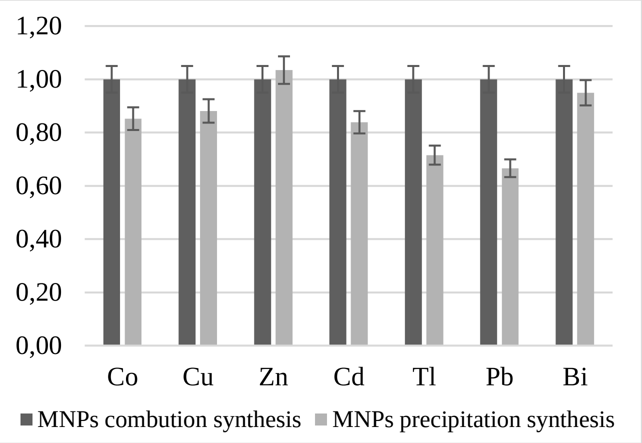

**Fig. 2.** Comparison of normalized signals for Co, Cu, Zn, Cd, Tl, Pb and Bi after MSPE with $MnFe_2O_4@SiO_2$-APDC synthesized by both approaches

In the present study, impregnation of MNPs with APDC is carried out at ambient temperature, unlike the conditions suggested by Meng *et al*, [20] where the authors carry out the process for the same time at 60° C. In our opinion the heating will lead to thermal decomposition of the APDC. The last is also supported by the fact that in order to increase extraction of Cu and Ni, the authors recommend introduction of an additional amount of ligand during SPE.

### *Optimization of solid phase extraction procedure*

The parameters influencing sorption of Co, Cu, Zn, Mo, Cd, Tl, Pb and Bi on the $MnFe_2O_4@SiO_2$-APDC NPs such as solution acidity and amount of the solid phase were evaluated by extraction degree (E%), based on ICP-MS determination of residual elements concentrations in aqueous phase after performing the SPE.

Comparison of the sorption properties of both types modified MNPs for group extraction of 7 elements from model solutions (10 μg $L^{-1}$) is presented on figure 2. The measured signals for tested elements in solution after extraction were normalized and used for estimation of sorption efficiency.

For all tested elements, except Zn and Bi, higher sorption efficiency was achieved using $MnFe_2O_4$ MNPs produced by the solution combustion method. The observed effect is probably due to the smaller size of these nanoparticles, which reflects on a larger sorption surface. Therefore, all subsequent studies were conducted with these nanoparticles.

The acidity of aqueous phase affects the stability of the metal-ligand complex formation. The extraction efficiency was studied in pH range of 3-8 (Fig.3). In a strongly acidic environment, the ligand may decompose to thiourea, whereas at pH > 9, it may be expected that the hydroxide-forming reactions of the target elements will compete.

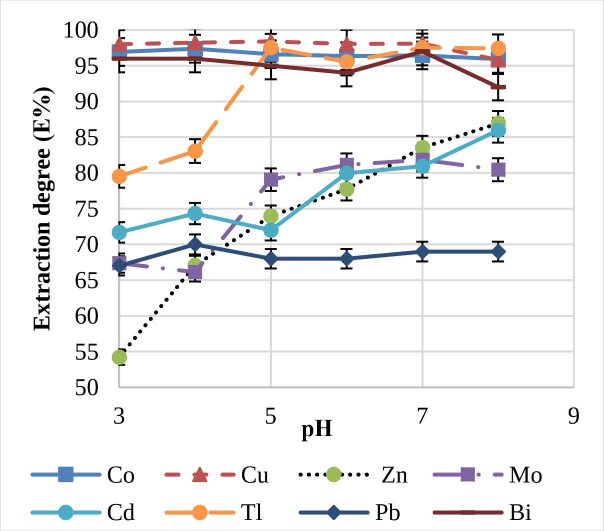

**Fig. 3.** Influence of the acidity of the aqueous phase on extraction

*Conditions: 30 mg sorbent, $C_A$ = 10 µg L$^{-1}$; $V_A$ = 50mL; $t_{extr}$ = 30min*

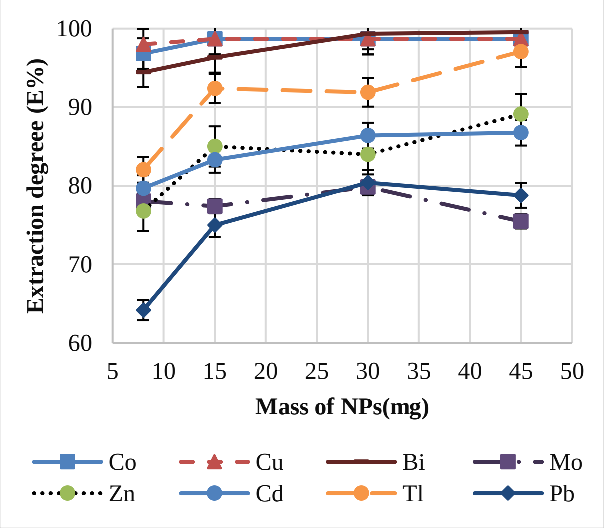

**Fig. 4.** Influence of the MNPs amount on extraction efficiency. Conditions: pH=5, $C_A$ = 10 µg L$^{-1}$; $V_A$ = 50mL; $t_{extr}$ = 30min

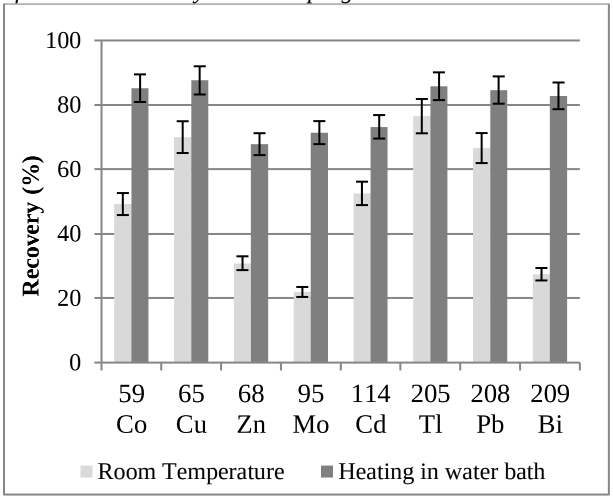

**Fig. 5.** Influence of the temperature on recoveries of tested elements using 1 mol L$^{-1}$ nitric acid as eluent

Three groups of elements could be distinguished according to their behavior at variation of pH. Three elements (i.e., Co, Cu, Bi) are extracted completely (E > 95%) regardless of the pH. Lead may also be added to this group, the extraction of which is also constant to the pH range tested, but does not exceed 70%. For Tl and Mo the extraction degree increases until pH = 5, then remains constant. The third group includes Zn and Cd and shows an increase in extraction efficiency across the whole range examined; hence for them is more beneficial to conduct extraction in basic medium. The commented above indicates that selectivity of sorbent could be improved by performing extraction at different pH but for the purpose of group solid phase extraction of all tested elements, pH = 5 was chosen as a compromise acidity for further experiments.

### *Optimization of the quantity of sorbent $MnFe_2O_4@SiO_2@APDC$*

The amount of nanoparticles used for SPE determined the contact surface between phases, as well as the amount of ligand introduced into the system. The influence of quantity of sorbent on solid phase extraction efficiency is studied varying the amount of NPs in the range of 8 mg to 45 mg (Figure 4).

Efficient extraction with E% ≥ 95% for Co, Cu and Bi and 78% for Mo could be achieved using only 8 mg modified NPs. For Tl, Cd, Zn and Pb, a raise in the extraction degree (by 8-14%) with a sorbent mass increase up to 30 mg was observed. For a group extraction 30 mg $MnFe_2O_4@SiO_2$-APDC was chosen as optimum.

### *Desorption studies*

The process of desorption of the analytes with a suitable solvent is estimated by their recovery (R%). In this case, a concentration of the elements in final solution, after performing of SPE and elution was measured.

In most of published investigations using APDC as complexing agent for SPE extraction, as best eluent an organic solvent (i.e acetonitrile [20]) or combination of acid and organic solvent i.e nitric acid and acetone [21] are proposed. In our case the organic eluents are inappropriate, considering the stability of inductively coupled plasma used for final measurement (namely ICP-MS). For this reason, dilute nitric acid with a volume of 3 ml and a concentration of 1 mol $L^{-1}$ was used to dissolve the APDC complexes of tested elements. The influence of temperature on the desorption process was studied, and the results from comparison of elution at room temperature for 30 minutes at continuous stirring and heating in boiling water bath for 15 minutes are presented on figure 5.

For all tested elements recovery is increased if the elution was performed at elevated temperature. The most affected by the elution temperature are results for Co, Zn, Mo and Bi. In order to achieve higher recovery and shorten the overall time for solid phase extraction, it was chosen to carry out desorption of the analytes by heating in boiling water bath for 15 minutes. Recoveries in the range of 68% (Zn) and 88% (Cu) were achieved for all studied elements.

### *Analytical characteristics of the developed ($MnFe_2O_4@SiO_2$-APDC)-ICP-MS method*

The analytical characteristics of the combined ($MnFe_2O_4@SiO_2$-APDC) - ICP-MS method were evaluated by analysis of the tested elements in calibration solutions passed through SPE on modified nanoparticles under optimized conditions (SPEcalib). The concentration of elements varied in the range of 5 to 20 µg $L^{-1}$ at three levels (5, 10 and 20 µg $L^{-1}$). The obtained coefficients of the calibration equations with their statistical evaluations as well as the achieved method limits of detection are presented in Table 2. The enrichment factors (EF) are calculated as the ratio of slopes for two calibration curves – the ones obtained when standard solutions were subjected to the SPE procedure (SPE calib) and when standards were prepared by spiking of aliquots in the 1 mol $L^{-1}$ nitric acid. Considering the concentration factor, calculated as the ratio of volumes of sample and eluent, is 16.6 the obtained EF confirmed that the optimized SPE procedure provides sustainable recoveries in studied concentration range. By using SPE calib as a calibration approach the losses due to the incomplete recoveries commented above can be adequately corrected.

During the ICP-MS measurement it was observed that signals measured in the final solution after extraction revealed a non-spectral matrix effect expressed in ~ 5 ÷ 10% suppression compared to the corresponding solutions prepared directly in dilute nitric acid (1 mol $L^{-1}$). The suppression obtained here is lower in comparison to the one reported in a previous work, where unmodified NPs were used for extraction of Me-APDC complexes, preliminary formed in solution (matrix suppression ~30%) [18]. The alleviation of matrix effect is due to a protective silica layer, which prevents the dissolution of magnetic core (containing Fe and Mn) during elution. For correction of the commented matrix impact as well as instrumental drift, only one internal standard (Rh) was added to the eluting acid.

The obtained high correlation coefficients (> 0.99 for all tested elements except for Zn and Mo), presented in table 2, proved that SPE of tested elements on APDC-impregnated silica modified magnetic nanoparticles is reproducible and applicable in studied concentration range. The intercept values of the regression equations for Co, Cu, and Pb are statistically distinguishable from zero because of the signals registered in blank sample, due to the presence of these elements in the precursor salts used for nanoparticle synthesis.

For validation of the combined ($MnFe_2O_4@SiO_2$-APDC)-SPE-ICP-MS method a surface water reference material SPS-SW1was analysed with both MNPs used as a solid phase. The extraction was performed under optimized conditions and SPE-calib approach was used for calibration and Rh as IS. The obtained results with corresponding uncertainties and certified values are presented on table 3.

The measured concentrations for Co, Cu, Cd, Tl and Pb are in good agreement with the certified values for both studied sorbents, which proves proved the reliability of the proposed magnetic NPs-SPE–ICP-MS procedure.

## CONCLUSIONS

The modified $MnFe_2O_4@SiO_2$-APDC nanoparticles are promising sorbent for SPE of trace elements. Core – shell modification with silica prevents the magnetic core from dissolution in acidic medium, which reduces non-spectral matrix effect in ICP-MS analysis.

A higher amount of silica reagent is necessary for modification in case of MNPs synthesized by SCS and preliminary treatment with nitric acid for eliminating unmodified fraction before impregnation is recommended. By proposed procedure for impregnation with APDC a successful extraction of Co, Cu, Zn, Cd, Tl, Pb and Bi could be performed without necessity of additional introduction of ligand during extraction.

**Table 2.** Analytical characteristics achieved with ($MnFe_2O_4@SiO_2$-APDC)-SPE-ICP-MS

| Isotope | slope<br>IS ratio x L x µg$^{-1}$ | ±SD<br>IS ratio x L x µg$^{-1}$ | Intercept<br>IS ratio | ±SD<br>IS ratio | Correlation coefficient | Enrichment factor (EF) | MLOD$^*$<br>µg L$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $^{59}$Co | 3.5 | ± 0.1 | 7.9 | ± 1.5 | 0.999 | 14.2 | 0.05 |
| $^{65}$Cu | 1.04 | ± 0.01 | 6.9 | ± 0.1 | 1.000 | 14.6 | 0.18 |
| $^{68}$Zn | 0.42 | ± 0.07 | 2.3 | ± 0.9 | 0.985 | 11.2 | 0.30 |
| $^{95}$Mo | 0.18 | ± 0.03 | 3.0 | ± 0.3 | 0.972 | 11.9 | 0.35 |
| $^{114}$Cd | 1.42 | ± 0.07 | -0.8 | ± 0.8 | 0.998 | 12.2 | 0.01 |
| $^{205}$Tl | 9.0 | ± 0.2 | 2.4 | ±2.7 | 0.999 | 14.3 | 0.01 |
| $^{208}$Pb | 3.4 | ± 0.3 | 57 | ± 3 | 0.995 | 14.1 | 0.67 |
| $^{209}$Bi | 5.9 | ± 0.2 | -0.3 | ± 2.8 | 0.998 | 13.8 | 0.02 |

*$^*$MLOD is calculated according to 3σ criteria using standard deviation of 5 independent measurements of blank and regression parameters obtained by SPE calib*

**Table 3.** Results from ($MnFe_2O_4@SiO_2$-APDC)-SPE-ICP-MS analysis of surface water reference material SPS-SW1 with both modified MNPs

| | Reference material SPS_SW 1 | | | | | |
|---|---|---|---|---|---|---|
| | Measured concentration | | | | Certified value | |
| Element | **$MnFe_2O_4@SiO_2$-APDC**<br>(co-precipitation)<br>µg L$^{-1}$ ±U | | **$MnFe_2O_4@SiO_2$-APDC**<br>(solution combustion)<br>µg L$^{-1}$ ±U | | µg L$^{-1}$ ±U | |
| Co | 1.84 | ±0.18 | 2.0 | ±0.2 | 2 | ±0.02 |
| Cu | 21.2 | ±1.7 | 18.5 | ±1.6 | 20 | ±1 |
| Cd | 0.52 | ±0.09 | 0.46 | ±0.06 | 0.5 | ±0.01 |
| Tl | 0.47 | ±0.02 | 0.47 | ±0.02 | 0.5 | ±0.01 |
| Pb | 4.79 | ±0.16 | 4.79 | ±0.15 | 5 | ±0.1 |

The elution at elevated temperatures improves obtained recoveries for all tested elements. The combined $MnFe_2O_4$ NPs-SPE–ICP-MS method proved to be effective for group determination of trace elements in water using SPE-calib approach and Rh as internal standards.

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