

# Amino and mercapto functionalized silica-modified magnetic nanoparticles for the preconcentration of heavy metals for ICP-OES analysis



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## 1. INTRODUCTION

Magnetically driven separation technology has received considerable attention in recent decade for its great potential in analytical chemistry [1,2]. Iron-oxide magnetic nanoparticles (NPs) have been showing a worldwide growing research interest as they possess unique size dependent characteristics that strongly differ from the properties of the corresponding bulk material and enable them to be used for numerous applications [3,4]. In this study, we investigate the application of bifunctional silica-modified magnetite NPs containing mercapto- and amino-groups for microextraction and determination of trace amounts of heavy metals from environmental water samples. The mercapto- and amino-groups were introduced on the silica modified magnetic nanoparticles using (3-mercaptopropyl)trimethoxysilane and (3-aminopropyl)trimethoxysilane, N-[3-(trimethoxysilyl)propyl]ethylenediamine, N-[3-(trimethoxysilyl)propyl] diethylenetriamine respectively.

The applicability of the nanomaterial was verified using a real sample matrix and the accuracy of the method was evaluated by recovery measurements on the spiked samples

## 2. MATERIAL AND METHODS

### 2.1 Synthesis of silica magnetic nanoparticles

Tetrahydrate iron(III) chloride 0.42g, hexahydrate iron(II) chloride 1.13g were mixed in 100mL of deoxygenated water, under vigorous stirring. The temperature was raised to 80°C and 5mL of 25% ammonia was added to form a black precipitate of magnetite NPs. The suspension was further heated for 30min under continuous flow of nitrogen and the magnetic nanomaterial was separated from the supernatant by a magnet. The particles were subsequently coated with TEOS. The procedure consisted of placing 25mL of ethanol and 8mL of DDW into a beaker containing 0.5mg of magnetite nanoparticles. Then, 1mL of ammonia and 500µL of TEOS were added following an overnight stirring, under nitrogen. After magnetic separation, the silanized magnetic particles were thoroughly washed with ethanol.

### Synthesis of amino and mercapto functionalized silica-modified magnetic nanoparticles

0.3g of silica magnetic nanoparticles were weighted in a beaker and 25ml toluene were added. Different ratios of (3-mercaptopropyl)trimethoxysilane and (3-aminopropyl)trimethoxysilane (product A), (3-mercaptopropyl)trimethoxysilane and N-[3-(trimethoxysilyl)propyl]ethylenediamine (product B) and (3-mercaptopropyl)trimethoxysilane and N-[3-(trimethoxysilyl)propyl] diethylenetriamine (product C) were added for the introduction of amino- and mercapto-groups.

The reaction took place in toluene under mild stirring at 100°C for 24h. The synthesized nanoparticles were characterized by BET, XRD, IR and SEM

### Study and optimization of the enrichment procedure

A screening and optimization study has been performed to assess the capacity of the nanomaterial to interact with metal ions and to come up with the best performance conditions. To optimize the designed procedure and set the criteria of selection, several factors were isolated from the different stages of analysis (extraction time and temperature, sample volume, slurry amount and state and ICP-OES measurement) and carefully investigated with synthetic aqueous sample solutions. For the method development, initial conditions with a sample volume of 50mL and an analyte concentration of 3.0µg L<sup>-1</sup> for each element have been used. 5mg of nanoparticle per sample were carried to the sample solution. All investigations were carried out with three fold replication.

### Preconcentration of metals and analysis

Aqueous samples with varying initial metal concentrations were used. All the experiments were carried out in 100mL capped bottles containing 50mL of standard solution (or sample) at 25°C and the nanoparticles were added in the form of a suspension. The initial pH of the solutions was adjusted to 6.0 or 8.0 by addition of 0.1N HNO<sub>3</sub> or 0.1N NaOH. The procedure was carried out in a contact time period of 30min with the concentration of nanomaterial to be at 5mg/50mL sample. Stirring was maintained at 350rpm to ensure quantitative extraction using an orbital shaker. Once equilibrium was reached, the nanosorbent with the retained analytes was harvested via an external magnetic field. The remaining particles were extracted with 2.5mL of 2N HNO<sub>3</sub>.

## 3. RESULTS AND DISCUSSION

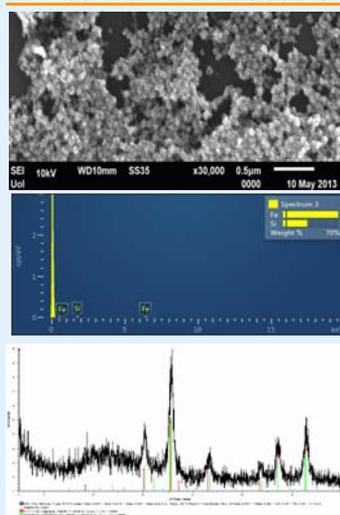


Figure S1. Scanning electron microscopy image, EDS and XRD of NPs

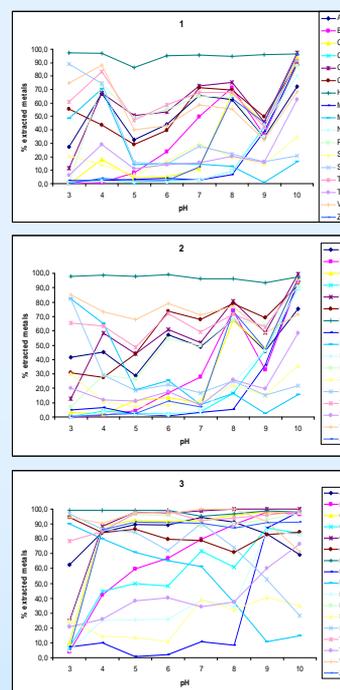


Figure 3. Effect of pH on the extraction of metals on products A,B and C.

## 4. CONCLUSION

A novel preconcentration procedure for the multielement enrichment prior to analysis with ICP-OES has been introduced in this study. The NPs synthesized in this study feature high capacity to interact with certain metal ions. By using 50mL of sample volume and 5mg of the magnetic nanomaterial, enrichment factors of 14 to 19 could be achieved. Compared to conventional solid-phase extraction this method includes advantages like simplicity, low cost and consumption of solvents. The NPs bearing the target metals are easily separated from the aqueous solution by applying an external magnetic field and the complexed metals are desorbed using HNO<sub>3</sub>. The proposed method is rapid with negligible sample preparation and offers good detection limits and acceptable precision for routine analysis of liquid environmental and biological samples. The desorbed metals are determined with ICP - OES. Under the optimized conditions, the detection limits are in the range 0.01 – 0.37µg/L.

## 5. ACKNOWLEDGEMENTS

This work was funded by the Republic of Cyprus (Research Promotion Foundation) and the EU structural funds under the programme "Functionalized magnetic nanocomposites in conjunction with atomic spectroscopy for the improved trace determination of heavy metals: Nano-ICP". The use of the XRD and SEM units of the Network of Research Units of the University of Ioannina is gratefully acknowledged.

Table 1.

Parameter	Value
pH	6 – 8
Temperature (°C)	25
Extraction time (min)	30
Stirring rate (rpm)	350
Sample volume (ml)	50
Nanomaterial (mg)	10

Table 2. Spectral lines of ICP-AES measurements, limits of quantitation and preconcentration factors for the studied metals

Analyte	Spectral line	LOQ (µg L <sup>-1</sup> )	Preconcentration factor
As	189.0	0.46	18
Be	313.0	0.15	19
Cd	226.5	0.05	18
Co	228.6	0.12	14
Cr	267.7	0.61	18
Cu	324.7	0.51	17
Hg	184.9	0.10	16
Mn	257.6	0.14	18
Mo	202.0	0.22	14
Ni	221.6	0.14	14
Pb	220.3	0.51	17
Sb	206.8	0.29	19
Se	196.0	0.24	19
V	292.4	0.23	19

Table 3. Mean concentrations (n = 3) of heavy metals in environmental and biological samples (µg L<sup>-1</sup>)

Analyte	Well water	Reservoir water	Urine
As	3.0±0.2	3.0±0.3	nd
Be	0.4±0.1	0.5±0.1	0.7±0.2
Cd	0.4±0.1	0.2±0.1	nd
Co	0.21±0.03	0.21±0.03	nd
Cr	0.12±0.03	nd	5.1±0.9
Cu	4.7±0.4	8.3±0.6	5.1±0.3
Hg	nd	nd	nd
Mn	1.1±0.2	1.4±0.3	0.9±0.1
Mo	1.9±0.1	1.3±0.3	4.9±0.3
Ni	19.7±0.4	3.2±0.3	nd
Pb	3.4±0.2	3.2±0.4	nd
Sb	4.3±0.3	2.2±0.2	nd
Se	20±1	2.1±0.2	23±1
V	23±1	7.2±0.3	nd

