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Automated magnetic sorbent extraction based on octadecylsilane functionalized maghemite magnetic particles in a sequential injection system coupled with electrothermal atomic absorption spectrometry for metal determination

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ABSTRACT

A new automatic sequential injection (SI) system for on-line magnetic sorbent extraction coupled with electrothermal atomic absorption spectrometry (ETAAS) has been successfully developed for metal determination. In this work, we reported effective on-line immobilization of magnetic silica particles into a microcolumn by the external force of two strong neodymium iron boron (NdFeB) magnets across it, avoiding the use of frits. Octadecylsilane functionalized maghemite magnetic particles were used as sorbent material. The potentials of the system were demonstrated for trace cadmium determination in water samples. The method was based on the on-line complex formation with diethyldithiocarbamate (DDTC), retention of Cd–DDTC on the surface of the MPs and elution with isobutyl methyl ketone (IBMK). The formation mechanism of the magnetic solid phase packed column and all critical parameters (chemical, flow, graphite furnace) influencing the performance of the system were optimized and offered good analytical characteristics. For 5 mL sample volume, a detection limit of 3 ng L^{-1}, a relative standard deviation of 3.9% at 50 ng L^{-1} level ($n=11$) and a linear range of 9–350 ng L^{-1} were obtained. The column remained stable for more than 600 cycles keeping the cost down in routine analysis. The proposed method was evaluated by analyzing certified reference materials and natural waters.

1. Introduction

The analysis of cadmium in natural water samples attracts considerable attention because of its increasing release into the environment, leading to serious pollution, particularly as a result of industrialization [1]. Cadmium exposure at low levels usually does not produce immediate health effects, but can cause adverse health effects over long periods. Cadmium is classified as a human carcinogen according to the U.S. Environmental Protection Agency [2]. World Health Organization (WHO) has established the upper permissible level of cadmium in drinking water as 3.0 μg L^{-1} [3].

Atomic spectrometric techniques are widely employed for the determination of metallic species at trace and sub-trace-level concentrations. Electrothermal atomic absorption spectrometry (ETAAS) is inherently characterized by remarkable sensitivity, although it suffers from matrix composition which can be overcome by the use of sample pretreatment techniques. On-line solid phase extraction (SPE) has several advantages over off-line operation considering the time of analysis and risk of contamination [4–6]. Thus, it has become one of the most commonly used and greenest alternative sample pretreatment techniques due to its simplicity, low cost, reduced sample and reagents consumption, high sensitivity and selectivity as well. The current research in SPE focuses on the development of novel efficient sorbent materials with large capacity [7,8] such as polytetrafluoroethylene (PTFE) [9,10], polyether–ether–ketone (PEEK) [11], reversed-phase poly(divinylbenzene-*N*-vinylpyrrolidone) co-polymeric beads (Oasis HLB) [12,13], carbon nanotubes [14,15] and magnetic particles [16,17], since the selection of the appropriate one is of prime importance for the sensitivity and selectivity of an analytical method.

Magnetic particles (MPs) commonly consist of magnetic elements such as iron, nickel, cobalt and their oxides. Superparamagnetic iron oxide (magnetite, Fe_3O_4 or maghemite, γ-Fe_2O_3) nano-particles (NPs), as a new kind of adsorbent in SPE, is gaining great interest in analytical atomic spectrometry for trace analysis over the last few years owning to their small size and high surface area providing better kinetics and greater extraction capacity as well as the ease of manipulation under the influence of an external magnetic field. Due to the fact that they can easily form large aggregates resulting in

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changes of their magnetic properties, modification of the reactive particles' surface with specific functional groups (organic or inorganic molecules) is usually needed. Moreover, surface modification stabilizes the NPs and prevents their oxidation. The modifying strategies applied to magnetic NPs (MNPs) can be classified into two categories depending on the presence of two major groups: inorganic components (e.g., silica coated) and organic molecules (e.g., modified with polymer or surfactant) [18]. Various magnetic materials have been reported as promising adsorbents for trace elements analysis such as silica coated MNPs modified with γ-mercaptopropyltrimethoxysilane (γ-MPTMS) for Cd, Cu, Hg and Pb [19], bismuthiol-II for Cr, Cu and Pb [20], iminodiacetic acid (IDA) immobilized on mesoporous Fe_3O_4@-SiO_2 microspheres (Fe_3O_4@SiO_2@IDA) for Cd, Mn and Pb [21], cetylpyridinium bromide (CPBr) cationic surfactant for Cu, Ni, Co, Cd, Pb and Mn [22] and dithizone (H_2Dz) for Cr(III), Cu, Pb and Zn [23]. In addition, Fe_3O_4 MNPs coated with decanoic acid were used for trace amounts of Cd, Co, Cr, Ni, Pb and Zn determination in environmental water samples [24]. Octadecylsilane (ODS) modified magnetic materials have been successfully used for organic compounds preconcentration [25,26] due to their favorable separation ability, excellent stability and long lifetime [27]. However, they have not been employed for metal determination.

The term of magnetic solid phase extraction (MSPE) was first introduced in batch mode by Šafaříková et al. [28] while Lee et al. [29] reported an on-line MSPE system for heavy metals determination using MNPs modified with polyacrylic acid (PAA) and ICP-MS as detector. In this work, an external permanent magnet and two were frits used to immobilize the MNPs–PAA in a cross section area into the microcolumn. Very recently, Wang et al. [17] proposed a sequential injection lab-on-valve (SI-LOV) system based on bead injection renewable column platform, followed by ETAAS. The method was demonstrated for cobalt determination using 1-(2-pyridylazo)-2-naphthol (PAN) loaded on sodium dodecyl sulfate (SDS) functionalized alumina coated Fe_3O_4 NPs, which were trapped inside a micro-channel, engraved on the LOV system, by using only one permanent magnet in contrast to the above work where two frits were necessary. An alternative approach for the packing of magnetic particles in on-line SPE systems was presented by Yan et al. [30] using a knotted reactor (KR) placed inside a tubular permanent magnet in order to retain the MPs instead of a column. An interesting approach for tackling the problems deriving from column packing was presented by Chen et al. [16] using a microfluidic chip manifold and two permanent magnets placed on each side of a microchannel in an exact distance in order to form a robust packed column. To our knowledge, it still remains a great challenge to hold the magnetic particles into a microcolumn without the use of frits or plugs in order an effective on-line SPE microcolumn with a practically unlimited lifetime to be formed.

In the present work, the above commented problems have been efficiently addressed by employing two strong neodymium magnets for on-line packing of a microcolumn with octadecylsilane (ODS) maghemite (Fe_2O_3) magnetic particles. To the best of our knowledge ODS–MPs have never been employed for metal determination so far. The proposed SI–MSPE system coupled with ETAAS was demonstrated for trace cadmium determination. All the important parameters of the proposed method were studied and optimized enhancing its effectiveness. The method was applied for the analysis of environmental samples.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer model 5100 PC atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA, http://las.perkinelmer.com) with Zeeman effect background correction and a transversely heated graphite tube atomizer (THGA), equipped with AS-71 furnace autosampler and a circulating cooling unit was employed throughout the measurements. Pyrolytically coated THGA graphite tubes (Perkin-Elmer) with integrated L'vov platform were used. Argon 99.996% was used as purge and protective gas. A Perkin-Elmer Lumina^{TM} single element hollow cathode lamp (HCL) for cadmium operated at 4 mA was used as a light source. The wavelength was set at 228.8 nm resonance line and the monochromator spectral bandpass (slit) was 0.7 nm. The graphite furnace temperature/time program for cadmium determination in IBMK includes preheating/drying steps at 90/110 °C as well as a pyrolysis step at 350 °C and summarized in Table 1. Integrated absorbance (peak area) was used for signal evaluation throughout the study.

A FIAlab$^{®}$-3000 sequential injection (SI) system (Alitea FIAlab, USA) equipped with an internally incorporated six-port multiposition valve (MV) was used for the automatic process of the proposed method. The SI system was controlled by a personal computer and the FIAlab application software for windows v. 5.9.245 (http://www.flowinjection.com).

Two additional micro-syringe pumps (MicroCSP-3000, FIAlab Instruments, Bellevue, WA), one with a capacity of 5.0 mL and the other with a capacity of 2.5 mL, equipped with a three-position Teflon/Kel-F valve each at the top of them, were employed to deliver the sample and the reagent solution respectively. The micro-syringe pumps were associated and controlled by the FIAlab$^{®}$-3000 SI system through the FIAlab application software v.5.9. The entire system was commanded by the computer that controlled the SI system, as has been reported elsewhere [31], namely, the computer of the 5100 PC operated as a "slave" of the computer of the FIAlab$^{®}$-3000 system.

The MSPE microcolumn, for analyte complex adsorption/preconcentration, was constructed in our laboratory by on-line packing of ~20 mg of ODS–MPs within a piece of a narrow PEEK tubing (50 mm length × 1.0 mm i.d.). Two external strong neodymium iron boron (NdFeB) permanent magnets (50 mm length × 15 mm width × 15 mm depth) with a magnetic force of 1.42 T were used for the on-line immobilization of the MPs into the column.

Three VICI AG (Valco International) three-section "Tee" type confluence connectors (CC) made of PEEK, with 0.5 mm i.d. bore size was used as shown in Fig. 1.

The length of PTFE tubing used for all connections was kept as short as possible in order to minimize the dispersion and dead volume in the proposed system.

An Orion EA940 pH-meter was used for pH measurements.

2.2. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water, produced by a Milli-Q system (Millipore, Bedford. USA, www.millipore.com), was used throughout.

Table 1
Graphite furnace temperature program for cadmium determination in 40 μL of MIBK, without modifier.

Step	Temperature(°C)	Ramp time(s)	Hold time(s)	Argon flow rate (mL min^{-1})
Preheating	90	5	10	250
Drying	110	10	20	250
Pyrolysis	350	20	40	250
Atomization	2200	0	5	0
Cleaning	2400	1	2	250

All cadmium standard solutions were prepared by appropriate stepwise dilution of 1000 mg L^{-1} Cd(II) stock standard solutions in 0.5 mol L^{-1} HNO_3 (Merck Titrisol) before use. The standard solutions and samples were acidified to 0.01 mol L^{-1} HNO_3 (pH ~ 2.0) by dilute HNO_3. The chelating reagent, 0.2% (m/v) diethyl-dithiocarbamate (DDTC) solution was prepared daily by dissolving appropriate amount of DDTC (Aldrich, www.sigmaaldrich.com/european-export.html) in ultra-pure water without any further purification. All glassware were rinsed with distilled water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution and rinsed again five times with ultra-pure water.

The accuracy of the developed method was evaluated by analyzing the following standard reference materials: NIST CRM 1643e (National Institute of Standard and Technology, Gaithersburg, MD, USA) containing trace elements in water; BCR 278-R (Community Bureau of Reference Brussels, Belgium) trace elements in mussel tissue and IAEA-433 (International Atomic Energy Agency, IAEA) marine sediment.

An amount of ca. 0.3 g of certified reference material (tissue or sediment) was precisely weighed into sealed Teflon vessels and wetted by nitric acid, followed by perchloric and hydrofluoric acids (only for sediments). The HNO_3–$HClO_4$–HF acid mixture was in a volume ratio of 3:2:1. The digestion procedure was carried out at 120–130 °C in a stainless-steel pressurized bomb according the manufacturer recommendations. After cooling down the system, the digests were properly diluted in ultra-pure water and used for the analysis.

Natural water samples ground, river and costal seawater, were collected from the area of Northern Greece. They were filtered through 0.45 μm membrane filters, acidified to 0.01 mol L^{-1} HNO_3 (ca. pH 2) with dilute HNO_3 and stored at 4 °C in acid-cleaned polyethylene bottles in order to determine the "dissolved metal" fraction.

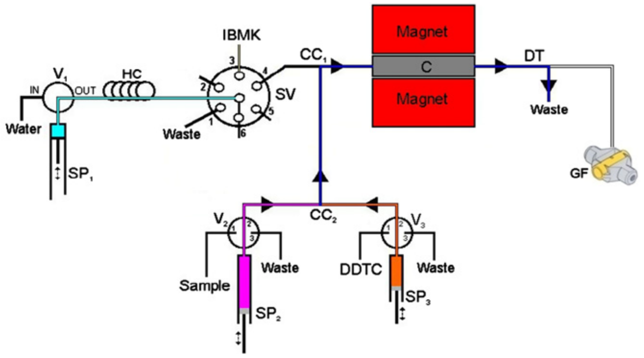

Fig. 1. Schematic diagram of the SI–MSPE–ETAAS system for cadmium determination. SV, selection valve; SP_1, SP_2, SP_3, syringe pumps; HC, holding coil; CC_1, CC_2, confluence connectors; DT, delivery tube; C, microcolumn; GF, graphite furnace of ETAAS; IBMK, isobutylmethylketone; DDTC, diethyldithiocarbamate.

2.3. Magnetic sorbent material

Octadecylsilane (ODS) functionalized maghemite (Fe_2O_3) ODS–MPs are commercially available in an aqueous dispersion solution with the product name SiMAG-Octadecyl and provided by Chemicell GmbH Germany (http://www.chemicell.com). These magnetic particles consist of a maghemite core and a matrix of non-porous silica functionalized with octadecyl (C18). The size of beads (hydrodynamic diameter) is 1.0 μm with a surface area of 50 m^2 g^{-1} and density of 2.25 g cm^{-3}. Their superparamagnetic properties make them easily separable by an external magnetic force. Moreover, the chemical modification of the silica surface with the octadecyl functional group allows a hydrophobic binding of hydrophobic substances.

2.4. On-line operating procedure

The schematic diagram of the SI system for the ETAAS determination of trace levels of cadmium is presented in Fig. 1 and the operation sequences are summarized in Table 2.

Each analytical cycle started with the aspiration of 5000 μL sample and 1250 μL reagent solutions into syringe pumps SP_2 and SP_3 respectively (step 1) and their simultaneous dispense through the confluence connector CC_1 towards the micro-column (C) where the on-line formed complex Cd(II)–DDTC retained on the surface of the ODS–MPs (step 2, preconcentration/sample loading). In step 4, a segment of 80 μL IBMK was aspirated into the holding coil (HC) in order to be used as eluent in step 5 (elution). Next, 280 μL were dispensed through the microcolumn by activating the SP_1 in order to transport the appropriate eluent segment up to the exit of the delivery tube (DT) after eluting the sorbent. As the injected volume of IBMK into the graphite tube (GF) should not be more than 40 μL, various portions of the 80 μL segment of IBMK were tested. Preliminary experiments revealed that the front 40 μL portion of the eluent contained the highest analyte amount. Therefore, in step 6, the DT, which was mounted at the arm of the autosampler of the ETAAS, moved into the dosing hole of the graphite tube and 40 μL of IBMK were dispensed for measurement. In step 7, the delivery tube (DT) moved to waste, and the atomization program of ETAAS which run in parallel with the SI program started. During the next steps (8–11), a thorough cleaning of the microcolumn and tubing was accomplished. The integrated absorbance signals were proportional to the cadmium concentration in the sample and used for

Table 2
Operational sequences of the SI–MSPE–ETAAS method for cadmium determination.

Step	Position				Operation			Flow-rate (μL s^{-1})			Volume (μL)			Commentary
	MV	V_1	V_2	V_3	SP_1	SP_2	SP_3	SP_1	SP_2	SP_3	SP_1	SP_2	SP_3	
1	4	OUT	1	1	–	Aspirate	Aspirate	–	100	50	–	5000	1250	Sample and reagent aspiration.
2	4	OUT	2	2	–	Dispense	Dispense	–	20	5	–	5000	1250	Preconcentration—Sample loading.
3	4	IN	–	–	Aspirate	–	–	50	–	–	500	–	–	Water into SP_1.
4	3	OUT	–	–	Aspirate	–	–	20	–	–	80	–	–	Segment of IBMK into HC.
5	4	OUT	–	–	Dispense	–	–	20	–	–	280	–	–	Elution—Transportation of the IBMK segment up to the exit of DT.
6	4	OUT	–	–	Dispense	–	–	5	–	–	40	–	–	DT into GF; 40 μL of the eluent injected into GF.
7														DT move to waste. Starting the ETAAS atomization program/ measurement.
8	4	OUT	–	–	Empty	–	–	20	–	–	–	–	–	Emptying of the HC.
9		IN	–	–	Aspirate	–	–	50	–	–	500	–	–	Water into SP_1.
10	3	OUT	–	–	Aspirate	–	–	30	–	–	400	–	–	IBMK into HC for cleaning the C.
11	4	OUT	–	–	Empty	–	–	20	–	–	–	–	–	Cleaning the C.

all measurements. Five replicate measurements were made in all instances.

The performance characteristics of the microcolumn and the MPs were consistent for at least 600 cycles without any decrease of the integrated absorbance.

3. Results and discussion

3.1. Packing of microcolumn with MPs

The effective packing of the microcolumn, the loss of sorbent material during the preconcentration, the steadily trapped and isoform distribution of the magnetic particles inside the column and the on-line column formation still remain a great challenge. Although some attempts solving relative problems and difficulties arising in on-line MSPE methods have been reported in the literature [16,29,30], more investigation on this topic is needed.

The critical factor to the formation of a well packed column is the attractive force of a very strong and uniform magnetic field to the MPs so as to avoid the creation of undesired canals inside the sorbent material. From preliminary investigations, it was obvious that in case of one magnet, the distribution of magnetic particles in the column was not uniform, resulting in poor reproducibility and low recovery of the analytes. When the dispersed solution of MPs was pumped into the column under the magnetic force of a single strong permanent magnet, the MPs followed the direction of the magnetic field lines, resulting in the formation of undesired canals inside the column even there was a small (Fig. 2a) or larger (Fig. 2b) amount of magnetic material. On the other hand, by using two strong permanent magnets in perpendicular position, the distribution became more uniform (Fig. 3a), and continuous introduction of MPs solution resulted in the formation of a well packed and steadily column, as shown in Fig. 3b.

Thus, the two permanent magnet configuration was adopted for effective packing of the column. The suspension of the MPs was introduced into the column by a peristaltic pump at a flow rate of 1.0 mL min^{-1} in a flow manifold as shown in the video (Video 1) in the supplementary material. When filled with the appropriate amount of MPs, the microcolumn along with the pair of magnets were fixed at the proposed SI system between the confluence connector CC$_1$ and CC$_3$, as shown in Fig. 1. It should be mentioned that the chemical and flow characteristics of the above packed column remained unchangeable for at least 600 analytical cycles and there was no need for reforming the column during the entire work. This is a silent advantage of the proposed method over the bead injection renewable column system [17] in which the MPs are being discarded after every analytical cycle.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.talanta.2013.02.035.

The adsorption capacity of ODS–MPs for cadmium was studied by equilibrating 20 mg of the sorbent with 100 mL of 10 mg L^{-1} Cd(II) including appropriate amount of DDTC for 1 h under vigorous stirring. Cadmium was determined in the filtrate by FAAS. The ODS–MPs' capacity was found to be 37 mg g^{-1}.

3.2. Optimization of chemical and flow parameters

All chemical and flow parameters related to the loading and elution steps of the SI–MSPE–ETAAS method were thoroughly studied using the univariate methodology so that the optimum analytical conditions could be reached. Standard aqueous solution of Cd(II) at 100 ng L^{-1} concentration level were used for the optimization study.

The selection of the appropriate eluent in on-line SPE systems is of prime importance in order to ensure complete and fast elution of the target analytes in a volume as small as possible. In case of ETAAS, an eluent should efficiently elute the retained complex in less than 50 μL; this volume is defined by the atomization requirements of the graphite furnace. Among ethanol, methanol and IBMK, the highest enhancement factors and the sharpest signals were obtained using IBMK as eluent, as has been proven elsewhere [32]. In a comparison study using ETAAS, the integrated absorbance obtained by metal chelate complexes in IBMK was found to be 10% higher than in 0.2% HNO$_3$ solution containing equal amount of metal, the background absorption was similar either for aqueous or organic solutions and no problems were encountered in injecting IBMK into the graphite tube [33]. In addition, in on-line SPE preconcentration systems, the use of IBMK as eluent may enhance the recorded signals by restricting the dispersion of the eluted analyte due to its hydrophobicity and immiscibility with water. Compared to IBMK, acidic solutions like hydrochloric acid and nitric acid in 2 mol L^{-1} concentration level were less effective as eluents. Thus, IBMK was adopted by modifying the atomization program, as shown in Table 1. Two preheating/drying steps were necessary for gradual drying of the organic solvent.

Among dithiocarbamate reagents which have been employed for chelation and preconcentration of trace metals, diethyldithiocarbamate (DDTC) and ammonium pyrrolidine dithiocarbamate (APDC) are the most widely used. These reagents behave as bidentate univalent anionic ligands having two donors S atoms, and form stable complexes with a large number of elements. The dithiocarbamate complexes are generally not soluble in water but dissolve readily in organic solvents like IBMK and chloroform. Although the above dithiocarbamates form extractable complexes in acidic sample solutions with cadmium, DDTC gives the highest absorbance, as it was proved elsewhere [34]. The effect of the concentration of the DDTC on the integrated absorbance was studied over the range 0.02–0.6% m/v. The recorded absorbance

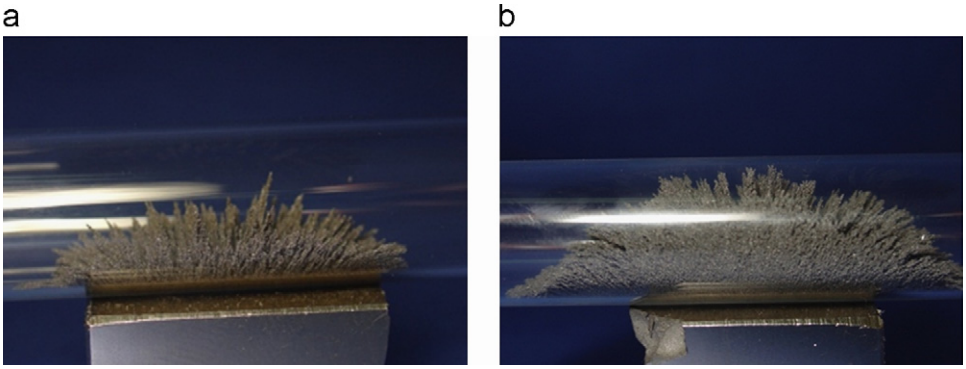

Fig. 2. Images of the distribution of the magnetic particles in the column through the packing process using only one permanent magnet. For details see the text.

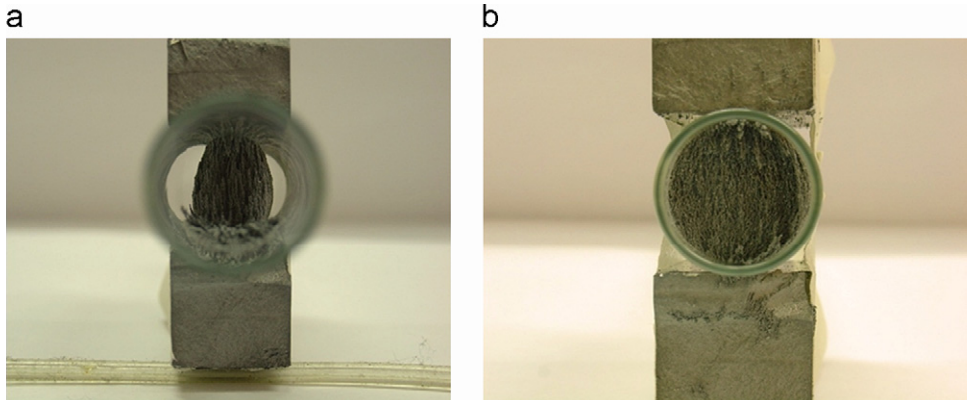

Fig. 3. Images of the distribution of the magnetic particles in the column through the packing process using two permanent magnets in perpendicular position. For details see the text.

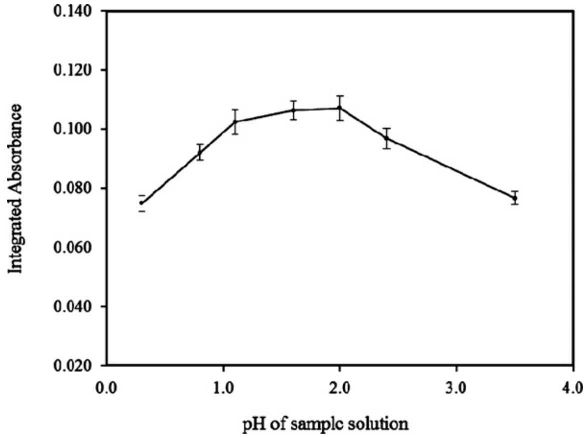

Fig. 4. Effect of pH sample on the integrated absorbance of 100 ng L^{-1} Cd(II). All other experimental parameters as in Table 2. Error bars calculated based on standard deviation values.

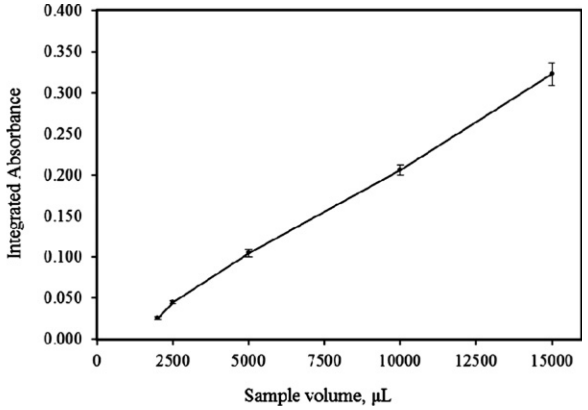

Fig. 5. Effect of sample volume on the preconcentration of 100 ng L^{-1} Cd(II). All other experimental parameters as in Table 2. Error bars calculated based on standard deviation values.

remained practical constant for DDTC concentration higher than 0.1% m/v. In the absence of the chelating agent, no detectable amount of cadmium could be retained in the column. Taking into account the competitive complexation of DDTC with other coexisting metals in natural water samples, a 0.2% m/v DDTC solution in water was adopted for subsequent studies.

The pH value of the sample or standard solution affects both complex formation and its retention on the sorbent material. The influence of pH on the integrated absorbance was studied over the range 0.2–3.5 adjusting it with dilute nitric acid. As can be seen in Fig. 4, quantitative adsorption was accomplished in the pH range 1.0–2.0. The low recovery at lower pH values was ascribed to the protonation of DDTC sulfate groups resulting in inefficient complex formation, while at higher values the integrated absorbance decreased probably due to possible hydrolysis. Thus, a pH value of 2.0 ± 0.2 was chosen for all subsequent experiments.

In on-line “volume based” preconcentration systems, the volume of the sample is the key factor affecting the sensitivity and the preconcentration rate of the method as well as the time of analysis. In order to evaluate the influence of the volume on the absorbance, it was studied in the range 2–15 mL. A general trend of practically proportional increased absorbance with increasing the sample volume was observed as shown in Fig. 5. Finally, 5 mL of sample solution was used for further studies as a compromise between sensitivity, time of analysis and low consumption of solutions.

The flow rate of sample solution affects the complex formation and its retention on the sorbent material as well as the time of analysis. Regarding the microcolumns packed with MPs, high flow rates tend to remove the particles from the column resulting in the disturbance of the uniformity inside it. The effect of sample flow rate was studied in the range 10–30 µL s^{-1} at a fixed DDTC flow rate 5 µL s^{-1}. The integrated absorbance was practically stable at flow rates up to 20 µL s^{-1}, while for higher values, a gradually decrease in the recorded signal was observed due to possible loss of material. Thus, a flow rate of 20 µL s^{-1} was employed for further studies.

The influence of eluent flow rate was also investigated over the range of 5–20 µL s^{-1} using the previous optimized conditions. It was found that the flow rate of the eluent had no obvious effect on the analytical performance. Thus, a flow rate of 20 µL s^{-1} was adopted considering the time of analysis.

3.3. *Evaluation of interferences*

The effect of potential interferences encountered in environmental samples on the preconcentration and determination of cadmium were studied under the optimized conditions. For this purpose a solution of 50 ng L^{-1} Cd(II) containing the corresponding interfering ion was prepared and analyzed with the proposed method. A variation on the recovery higher than ±5% was considered as interference. Experimental results revealed that the method could tolerate Al(III), Co(II), Cr(III), Cr(IV), Fe(III), Mn(II) and Zn(II) at concentrations up to 5 mg L^{-1}, while Cu(II), Pb(II) and Hg(II) up to 1 mg L^{-1}. In addition, commonly encountered matrix components in natural water samples alkaline and alkaline–earth metals, namely, Ca(II), Mg(II), Ba(II), Na(I) and K(I) were also examined. No significant variation in the recorded signals was observed at concentrations up to 500 mg L^{-1} of the above cations and also at concentrations up to 30 g L^{-1} of NaCl. Therefore, this fact makes the proposed on-line preconcentration system suitable for analysis of seawater.

3.4. Analytical features

The analytical performance characteristic data of the developed on-line SI–MSPE–ETAAS method for the determination of cadmium under the optimal conditions are summarized in Table 3. For sample consumption of 5 mL, the sampling frequency and the enhancement factor (calculated by the ratio of the slopes of the calibration curves obtained with and without preconcentration by direct injection of 40 μL of aqueous standard solution) were 8 and 19, respectively.

The detection limit (c_L), based on the 3*s* criterion (according to IUPAC [35]) was calculated as three times the standard deviation of the blank solution measurements ($n=11$) divided by the slope of the corresponding calibration curve and found to be 3 ng L^{-1}, while the precision of the method, expressed as relative standard deviation (RSD), was 3.9% at 0.05 μg L^{-1} Cd(II) concentration level. The method has a good precision and a suitable dynamic linear range from 9 to 350 ng L^{-1} with correlation coefficient (r) of 0.9979.

For comparative purposes, the analytical performance characteristics of selected on-line SPE methods with different sorbent materials for cadmium determination with atomic spectrometric techniques are given in Table 4. The proposed method appears good sensitivity and precision with similar detection limits with earlier works for cadmium by ICP–MS [36–38] and better performance compared to FAAS, ICP–AES and ETAAS [39,43–45,47]. Only one ETAAS method [46] provides better detectability.

In order to evaluate the accuracy of the proposed SI–MSPE–ETAAS method it was applied to the determination of cadmium in three standard reference materials, NIST CRM 1643e, BCR 278-R, and IAEA-433. Student *t*-test was employed to examine possible statistically significant differences between the recorded results and the certified values of the determined metals. The analytical values and $t_{\text{exp,}}$ values for Cd, determination in the above CRMs are given in Table 5. Since all $t_{\text{exp,}}$ values are lower than the $t_{\text{crit, }95\%}=4.30$, no

Table 3
Analytical performance characteristics of the SI–MSPE–ETAAS method for cadmium determination under the optimized conditions.

Sample consumption (mL)	5
Sampling frequency (h^{-1})	8
Enhancement factor	19
Regression equation (7 standards; $n=5$; [Cd] in ng L^{-1})	$A=(9.1\times10^{-4}\pm5.9\times10^{-5})$ [Cd]$+(4.2\times10^{-3}\pm1.2\times10^{-2})$
Linear range (ng L^{-1})	9–350
Detection limit, c_L (μg L^{-1})	3
Precision, RSD, % ($n=10$)	3.9 (at 50 ng L^{-1})
Correlation coefficient (r)	0.9979

Table 4
Comparison of analytical performance of the developed method with selected on-line SPE methods for cadmium determination with atomic spectrometric techniques.

Sorbent material/ligand	Detection system	Eluent	SC (mL)	c_L (ng L^{-1})	$s_{r\,(\%)}$	h^{-1}	EF	Ref.
Bond Elut Plexa PCX	FAAS	1.0 mol L^{-1} HCl	18.0	100	2.9	30	90	[39]
Alumina modified with SDS and 1,10-phenanthroline	FAAS	Ethanol	20.0	140	2.2	14	116	[40]
Polystyrene/NAPdein	FAAS	1.0 mol L^{-1} HNO_3	10.0	250	5.1	20	50	[41]
MWCNs/DDTC	FAAS	0.01 mol L^{-1} HNO_3	16.5	240	3.2	16	54	[15]
XAD-4-DHB	TS-FF-AAS	1.0 mol L^{-1} HNO_3	–	28	4.8	40	102	[42]
HypersepSCX	ICP–AES	2.0 mol L^{-1} HCl	15.6	70	4.5	24	13.2	[43]
Chitosan modified ordered mesoporous silica	ICP–AES	1.0 mol L^{-1} HCl	6.0	50	4.0	10	20	[44]
PVC beads	ICP–MS	0.5% HNO_3	0.1	2.7	–	–	10	[36]
PMMA beads	ICP–MS	0.5% HNO_3	0.1	5.0	–	–	–	[37]
PSTH-cpg	ICP–MS	4% HNO_3	1.8	4.0	–	8.6	2.4	[38]
PTFE	ETAAS	Ethanol/0.5% Triton X-100	1.25	5.5	1.3	12	20.6	[45]
Mungbean coat	ETAAS	1.0 mol L^{-1} HNO_3	1.4	1.4	2.4	8	20	[46]
AMSG	ETAAS	2.0 mol L^{-1} HNO_3	30	5.1	2.3	–	–	[47]
Cyanex 923	AFS	1% H_2SO_4	25	10.8	0.97	40	–	[48]
ODS–MPs/DDTC	ETAAS	IBMK	5	3.0	3.9	8	19	[a]

[a] This work; SC: sample consumption, c_L: detection limit; s_r: relative standard deviation; h^{-1}: sampling frequency; EF: enhancement factor; SDS: sodium dodecyl sulfate; NAPdein: *N*,*N*-bis(naphthylideneimino)diethylenetriamine; MWCNs: multi-wall carbon nanotubes; XAD 4-DHB: Amberlite XAD-4 functionalized with 3,4-dihydroxybenzoic acid; PMMA: poly(methyl methacrylate; PSTH-cpg: 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl controlled pore glass; PTFE: poly(tetrafluoroethylene); ODS–MPs: octadecylsilanized magnetic particles; TS-FF-AAS: thermospray flame furnace atomic absorption spectrometry; AMSG: Aliquat-336 modified silica gel; AFS: atomic fluorescence spectrometry.

Table 5
Validation of the proposed SI–MSPE–ETAAS method for cadmium determination in CRMs.

CRM	Certified value	Units	Found*	Relative error (%)	t_{exp}
CRM 1643e (Trace element water)	6.568 ± 0.073	μg L^{-1}	6.2 ± 0.4	5.6	1.593
BCR 278-R (Mussel tissue)	0.348 ± 0.007	mg kg^{-1}	0.34 ± 0.02	2.3	0.693
IAEA-433 (Marine sediment)	0.153 ± 0.033	mg kg^{-1}	0.15 ± 0.01	2.0	0.520

* Mean value ± standard deviation based on three replicates; $t_{\text{crit.}}=4.30$ at 95% probability level.

Table 6
Analytical results of cadmium determination in natural waters by the SI–MSPE–ETAAS method.

Sample	Added[a]	Found[a]	*R* (%)
Ground water	–	$< c_{\mathrm{L}}$	–
	50	49 ± 4	98
	100	95 ± 9	95
River water	–	$< c_{\mathrm{L}}$	–
	50	48 ± 3	96
	100	98 ± 8	98
Coastal seawater[b]	–	900 ± 75	–
	100	995 ± 69	95
	500	1386 ± 90	97

[a] Concentrations in ng L^{-1}, mean value ± standard deviation ($n=3$).
[b] After a 5-fold (1:5) dilution; *R*, recovery.

statistically significant differences were found at the 95% probability level, indicating the applicability of the developed method for metal determination in similar type of samples. The method was also applied to the analysis of ground water, river water and costal seawater. The results are presented in Table 6. The recoveries varied within the range 94–98% showing the good performance of the proposed method for the analysis of natural waters.

4. Conclusions

An automatic SI–MSPE system coupled with ETAAS has been developed using octadecylsilane (ODS) functionalized maghemite MPs as a novel sorbent material for preconcentration and determination of trace metals. The effectiveness and efficiency of the proposed methodology was successfully demonstrated for cadmium determination and applied in environmental samples.

The effective and robust on-line packing of the magnetic material into the microcolumn was achieved by the use of two strong neodymium magnets placed across it, without the need of any frits or other units. The excellent chemical and mechanical stability along with the long lifetime (more than 600 sorption/elution cycles) of the proposed microcolumn are important advantages for keeping the process cost down, in routine analysis. This extraction technique in the SI–MSPE format enabled a simple manifold, low sample and reagents consumption as well as high sample throughput.

References

[1] M. Miro, J.M. Estela, V. Cerda, Talanta 63 (2004) 201.
[2] U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Cadmium, National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1999.
[3] World Health Organization, Guidelines for Drinking-water Quality, vol. 1 Recommendations, 3rd ed., World Health Organization, Geneva, 2008.
[4] J.D. Butcher, Appl. Spectros. Rev. 41 (2006) 15.
[5] M. Miro, H.M. Oliveira, M.A. Segundo, Trends Anal. Chem. 30 (2011) 153–164.
[6] A.N. Anthemidis, M. Miro, Appl. Spectrc. Rev. 44 (2009) 140.
[7] V.A. Lemos, L.S.G. Teixeira, M. de A. Bezerra, A.C. Spínola Costa, J.T. Castro, L.A.M. Cardoso, D.S. de Jesus, E.S. Santos, P.X. Baliza, L.N. Santos, Appl. Spectrosc. Rev. 43 (2008) 303.
[8] D. Das, U. Gupta, A.K. Das, Trends Anal Chem. 38 (2012) 163.
[9] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, J. Anal. At. Spectrom. 17 (2002) 1330.
[10] X. Long, R. Chomchoei, P. Gała, E.H. Hansen, Anal. Chim. Acta 523 (2004) 279.
[11] A.N. Anthemidis, I.S.I. Adam, G.A. Zachariadis, Talanta 81 (2010) 996.
[12] A.N. Anthemidis, V. Cerdà, M. Miró, J. Anal. At. Spectrom. 25 (2010) 1717.
[13] A.N. Anthemidis, G. Giakisikli, S. Xidia, M. Miró, Microchem. J. 98 (2011) 66.
[14] C.H. Latorre, J.A. Mendez, J.B. Garcia, S.G. Martin, R.M.P. Crecente, Anal. Chim. Acta 749 (2012) 16.
[15] A.N. Anthemidis, M. Paschalidou, Anal. Lett. 45 (2012) 1098.
[16] B. Chen, S. Heng, H. Peng, B. Hu, X. Yu, Z. Zhang, D. Pang, X. Yue, Y. Zhu, J. Anal. At. Spectrom. 25 (2010) 1931.
[17] Y. Wang, X. Luo, J. Tang, X. Hu, Q. Xu, C. Yang, Anal. Chim. Acta 713 (2012) 92.
[18] K. Aguilar-Arteaga, J.A. Rodriguez, E. Barrado, Anal. Chim. Acta 674 (2010) 157.
[19] C. Huang, B. Hu, Spectrochim. Acta, Part B 63 (2008) 437.
[20] J.S. Suleiman, B. Hu, H. Peng, C. Huang, Talanta 77 (2009) 1579.
[21] N. Zhang, H. Peng, S. Wang, B. Hu, Microchim. Acta 175 (2011) 121.
[22] A.E. Karatapanis, Y. Fiamegos, C.D. Stalikas, Talanta 84 (2011) 834.
[23] G. Cheng, M. He, H. Peng, B. Hu, Talanta 88 (2012) 507.
[24] M. Faraji, Y. Yamini, A. Saleh, M. Rezaee, M. Ghambarian, R. Hassani, Anal. Chim. Acta 659 (2010) 172.
[25] S. Zhang, H. Niu, Y. Cai, Y. Shi, Anal. Chim. Acta 665 (2010) 167.
[26] Y. Liu, H. Li, J.-M. Lin, Talanta 77 (2009) 1037.
[27] L. Chen, T. Wang, J. Tong, Trends Anal. Chem. 30 (2011) 1095.
[28] M. Šafaříková, I. Šafařík, J. Magn. Magn. Mater. 194 (1999) 108.
[29] P.-L. Lee, Y.-C. Sun, Y.-C. Ling, J. Anal. At. Spectrom. 24 (2009) 320.
[30] Y.F. Huang, Y. Jiang, X.-P. Yan, J. Anal. At. Spectrom. 25 (2010) 1467.
[31] A.N. Anthemidis, K.-I.G. Ioannou, Anal. Chim. Acta 668 (2010) 35.
[32] M. Sperling, X-P. Yan, B. Welz, Spectrochim. Acta B 51 (1996) 1891.
[33] M. Gonzalez, M. Gallego, M. Valcarcel, J. Anal. At. Spectrom. 14 (1999) 711.
[34] I.S.I. Adam, A.N. Anthemidis, Talanta 77 (2009) 1160.
[35] International Union of Pure and Applied Chemistry (IUPAC), Compendium of Analytical Nomenclature, Definitive Rules 1997, 3rd ed., Blackwell, Oxford, 1998.
[36] C.-K. Su, T.-W. Lee, Y.-C. Sun, J. Anal. At. Spectrom. 27 (2012) 1585.
[37] T.-T. Shih, W.-Y. Tseng, K.-H. Tsai, W.-Y. Chen, M.-W. Tsai, Y.-C. Sun, Microchem. J. 99 (2011) 260.
[38] I.S. Trujillo, E.V. Alonso, A.G. de Torres, J.M.C. Pavón, Microchem. J. 101 (2012) 87.
[39] A.N. Anthemidis, S. Xidia, G. Giakisikli, Talanta 97 (2012) 181.
[40] A.M.H. Shabani, S. Dadfarnia, Z. Dehghani, Talanta 79 (2009) 1066.
[41] M.A. Chamjangali, S.T. Farooji, B. Bahramian, J. Hazard. Mater. 174 (2010) 843.
[42] V.A. Lemos, M.A. Bezerra, F.A.C. Amorim, J. Hazard. Mater. 157 (2008) 613.
[43] A.N. Anthemidis, G Giakisikli, G.A. Zachariadis, Anal. Methods 3 (2011) 2108.
[44] D. Chen, B. Hu, C. Huang, Talanta 78 (2009) 491.
[45] X. Long, R. Chomchoei, P. Gała, E.H. Hansen, Anal. Chim. Acta 523 (2004) 279.
[46] Y. Tian, Z.-M. Xie, M.-L. Chen, J.-H. Wang, J. Anal. At. Spectrom. 26 (2011) 1408.
[47] Y. Li, G. Hou, B. Zho, Y. Wei, At. Spectrosc. 33 (2012) 130.
[48] T. Duan, X. Song, D. Jin, H. Li, J. Xu, H. Chen, Talanta 67 (2005) 968.