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An ion imprinted magnetic organosilica nanocomposite for the selective determination of traces of Cd(II) in a minicolumn flow-through preconcentration system coupled with graphite furnace atomic absorption spectroscopy†

Yanina Susana Minaberry,** a Cecilia Costa, b Virginia Dizb and Mabel Tudinoa

In this paper we present the determination of ultratrace cadmium ions in water by means of a minicolumn (MC) flow-through preconcentration system coupled with graphite furnace atomic absorption spectrometry. The core of the system is a lab-made ion imprinted magnetic organosilica nanocomposite which is employed as filler of the MC for the selective retention of the analyte. In this case superparamagnetic magnetite nanoparticles were coated with an amine-functionalyzed shell and ion imprinted with Cd(II) by a simple sol–gel co-condensation method. The setup was completed with the inclusion of a magnet fixed around the packed MC. This assembly—which is studied with an MII material for the first time here—allowed a homogeneous distribution of the solid on the walls of the MC, leaving a hole in the center and enabling the absence of material bleeding or obstructions to the free movement of fluids. Ion imprinted (MII) and non-imprinted (MNI) materials were studied for comparison purposes. Both were characterized and compared by DRX, FTIR, TGA and their magnetic behavior by magnetization curves. Batch experiments showed an equilibration time of less than 10 minutes and a maximum adsorption pH of around 7 for both solids. The maximum capacity for MII was greater than that of MNI (200 mg g⁻¹ and 30 mg g⁻¹ respectively) and thus, the former was chosen for analytical purposes. Under MC dynamic conditions, sample and elution flow rates, volumes of the sample and eluant, and type and concentration of the most suitable eluant have been thoroughly investigated and optimized. Under the optimal experimental conditions, the MII filler showed a preconcentration factor of 200, a limit of detection of 0.64 ng L⁻¹, a linear range of 2.5–100 ng L⁻¹, RSD% of 1.9 (n = 6; 10 ng L⁻¹) and a lifetime of more than 800 cycles of concentration–elution with no loss of sensitivity or need for refilling. The effect of potentially interfering ions on the percent recovery of cadmium was also studied. The proposed method was successfully applied to the determination of traces of Cd(II) in osmosis and tap water with recoveries of 98.0–101.3%. A comparison with similar methods is also provided.

1. Introduction

Cadmium has been classified as one of the six most harmful elements for human health. Because of this, the WHO has set the maximum limit for drinking water at very low levels.1–3 This is why the determination of extremely low concentrations of toxic ions like bioavailable Cd(II) has given great importance to preconcentration techniques in modern analytical chemistry.4,5 Among these techniques SPE (Solid Phase Extraction) has been one of the most widely used due to its simplicity, flexibility, low consumption of solvents and reagents and high preconcentration factors.4–6

The influence of the analyte–sorbent interaction on the selectivity, affinity and retention capacity for achieving analyte isolation and efficient preconcentration in SPE has generated an increasing need for improving the design of solid supports.7–9

In particular, magnetic solid phase extraction (MSPE) is a SPE method that uses functionalized magnetic nanoparticles (MNPs) as sorbents owing to their magnetic advantages.10–12

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Due to magnetism, MNPs can be rapidly separated from aqueous samples using a magnet, thus avoiding centrifugation or filtration. The surface coating of MNPs not only prevents oxidation but also provides active sites for adsorption. MNPs are easily coated with inorganic materials (e.g., silica, titanium dioxide, and alumina) or organic polymers and then modified with functional groups to anchor in the pores and prevents pore blocking. However, these modified nanoparticles have been applied in non-specific adsorption of heavy metals due to a lack of selectivity. To improve the selectivity of the recognition process, ion-imprinted polymers (IIPs), similar to molecularly imprinted polymers (MIPs), have received widespread attention. This technique allows precise control of the stereochemical arrangement of ligands at the adsorption sites and thus, a selective recognition capability toward a given molecule/ion target.\textsuperscript{10,11,19,21}

In recent years, silica-coated MNPs with II have been widely investigated because, in addition to keeping their magnetic properties, they show an improvement in chemical stability and high selectivity for the target ion.\textsuperscript{20–24}

Regarding the synthesis of these composites, the sol–gel method is the most widely used. In particular, the use of the so-called one-pot method or co-condensation with imprinting offers advantages over the grafting method in terms of the increase of surface area, equilibrium adsorption capacity and kinetics. This is due to the simultaneous addition of the silica and template precursor and the structuring agent which allows the functional groups to anchor in the pores and prevents pore blocking.\textsuperscript{25–27}

However, these MNPs with II have been used exclusively in batch MSPE systems with known disadvantages such as high time and reagent consumption, large sample handling in magnetic separation, loss of analyte, contamination, etc.\textsuperscript{25–29}

In the case of non-imprinted coated MNPs, many efforts have been made to overcome these drawbacks by using different on- and off-line dynamic SPE systems. These are a more environmentally friendly alternative due to their simplicity, low cost, reduced sample and time consumption, increased sampling productivity, high sensitivity and selectivity.\textsuperscript{30–33}

In this regard our group has been devoted to studying SPE in flow-through systems holding an MC with filler materials (with and without II) in the last few years.\textsuperscript{34,35}

In this sense, different arrangements of flow systems using magnetic filler materials immobilized by the action of a permanent magnetic field have been sporadically reported in the literature. Problems related to material bleeding or need for reloading between measurements discourage this approach.\textsuperscript{30,36–40}

In this work we propose for the first time the use of magnetic materials with ion imprinting as filler materials of an MC held in a flow-through system for the preconcentration of Cd(II) followed by an optimized release and determination by GFAAS.

For comparison purposes imprinted (MII) and non-imprinted (MNI) composite materials were easily synthesised and employed as fillers in the MC. Both of them kept their superparamagnetic properties. The MII material showed higher selectivity and thus, a better analytical performance for both batch and continuous flow systems, including a lifetime of 800 analytical cycles.

Moreover, this novel and simple experimental setup, which employs a single circular magnet around the MC, allows a homogeneous distribution of the solid on the walls of the column, immobilises the magnetic nanoparticles and avoids in this way any physical barrier to their retention.

All these advantages are reflected in the comparison of its performance with other methods in the determination of Cd(II) by GFAAS. Furthermore, the applicability of the developed method was demonstrated by the determination of Cd(II) in real water samples.

2. Experimental

2.1. Reagents

Standard solutions of Cd(II), Zn(II), Ni(II), Pb(II), Co(II), Na(i), Cl\(^-\) and NO\(_3\)- were prepared by proper dilution of 1000 g L\(^{-1}\) stock standard solutions (Merck Darmstadt, Germany) with double deionized water, DDW (18 M\(\Omega\) cm\(^{-1}\), Milli-Q Water System, Millipore, Bedford, MA, USA). The pH of the solutions was changed through the addition of suitable quantities of HCl or NaOH solutions (Merck) (1 mol L\(^{-1}\)).

For the synthesis of magnetite, the following reagents were used: FeCl\(_2\)·4H\(_2\)O 99.0% (Sigma-Aldrich, Steinheim, Germany), FeCl\(_3\)·6H\(_2\)O 99.0% (Sigma-Aldrich, St Louis, USA) and ammonia solution 25% (Merck Darmstadt, Germany).

Tetaethylorthosilicate (TEOS) 98%, cetyl trimethylammonium bromide (CTAB) (\(M = 364.46\) g mol\(^{-1}\)) and 3-aminopropyltrimethoxysilane (APTES) from Sigma-Aldrich (Steinheim, Germany) were employed for magnetite functionalization and imprinting.

All operations were performed in a laminar flow hood. Nalgene glassware (Nalge, Rochester, NY, USA) was washed with a nitric acid solution (1 : 2) and rinsed with DDW, ethanol and acetone.

2.2. Apparatus

A pH-meter (Boeco BT-500, Germany) with a glass working electrode and a reference electrode of Ag/AgCl was used for pH measurements. FTIR spectra were collected using a NICOLET 8700 20 SXC spectrometer (Thermo Fisher). SEM micrographs were taken using a Zeiss DSM 982 Gemini (Carl Zeiss, Jena, Germany).

A vibrating sample magnetometer (LakeShore 7400 VSM, Lake Shore Cryotronics, Inc., USA) was used for the measurement of the magnetic properties of the material.

The flow-through measurements were performed using a peristaltic pump (IPC, Ismatec, Glattbrugg-Zürich, Switzerland), 0.5 mm i.d. PTFE\(^{\oplus}\) tubing (Cole Parmer, Chicago, IL, USA), and acrylic minicolumns (MC) fixed to the PTFE\(^{\oplus}\) tubing through 0.25–28 female connectors.

FAAS determinations of cadmium in batch experiments were carried out by running the standard program of the Shimadzu


AA 6800 (Shimadzu, Kyoto, Japan) spectrometer. A Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory (GFA 6000) and an autosampler (ASC-6000) was used for the determination of Cd(II) after preconcentration. A cadmium hollow cathode lamp (Hamamatsu Photonics, Japan), deuterium lamp background correction and pyrolytic graphite furnaces were employed throughout the measurements. Temperature programs were those provided by the manufacturer. For comparison of the determination of Cd(II) in natural waters, an ICP coupled to an MS (PerkinElmer SCIEX model ELAN DRC II, Thornhill, Canada, LOD = 50 ng L⁻¹) was employed. The operating conditions were those suggested by the manufacturer.

2.3. Sample preparation

Tap water from our laboratories and osmosis water samples provided by dialysis treatment centers from Argentina were stored in a low-density polyethylene bottle, and kept in a refrigerator at 4 °C. No sample pretreatment was performed before analysis.

2.4. Procedures

2.4.1. Synthesis of MII and MNI. First, Fe₃O₄ magnetic nanoparticles were prepared using a similar procedure reported in a previous study.⁴¹

MII and MNI were prepared via a one-step process as reported in a previous study except for some modifications that were introduced this time (see Fig. 1).²³ 55 mg CdCl₂-2.5H₂O and 220 mg APTES were dissolved in 10 mL DDW under stirring for 2 h at 60 °C to form a pre-assembly solution. Next, 0.53 g of CTAB was dissolved in 55 mL of ethanol 40% under stirring for 0.5 h. Then, the pre-assembly solution was added to this mixture and stirred for another 0.5 h. In parallel, 2.8 g of ammonia aqueous solution (25 wt%) was dissolved in 110 mL of DDW and stirred at 30 °C. Then, 100 mg of Fe₃O₄ was added to this ammonia solution and vigorously stirred for 0.5 h. After that, the above solution was added to this mixture and stirred for another 0.5 h. Then, 1.08 g of TEOS was introduced dropwise into the mixture under vigorous and continuous stirring for 24 h. The MII product was separated by a magnet, and rinsed with ethanol and DDW in succession.

To remove Cd²⁺ from the product, an ethanol/HCl solution (9 : 1, v/v) was used until no cadmium was detected in the supernatant. The resulting magnetic materials were neutralized with 0.1 mol L⁻¹ NaOH to pH 7, washed with DDW, centrifuged and dried at 60 °C for 24 hours using an identical procedure, except for the addition of CdCl₂-2.5H₂O.

2.4.2. Batch sorption experiments. Batch adsorption experiments were carried out by soaking 10 mg MNI and MII materials in 10 mL of a Cd solution at room temperature with mechanical stirring. After each adsorption experiment, the MII or MNI was separated by a magnet, and the residual concentration of Cd²⁺ in the supernatant was determined by FAAS.

With the aim of evaluating the influence of pH on the sorption of Cd(II), HCl, NH₃ or NaOH solutions were employed for pH conditioning (pH 1 to 8).

For determining the effect of the analyte/composite material contact time, experiments were carried out at the optimum pH, room temperature and definite intervals. Results were modelled with pseudo first order (PO1) and pseudo second order (PO2) models, according to Chiron et al.⁴² For pH sorption and kinetic studies the Cd(II) concentration was 5 mg L⁻¹.

The experiments to obtain the adsorption isotherms were carried out at initial Cd concentrations in the range 5–900 mg L⁻¹ at the optimum pH. The well-known adsorption isotherm model namely Langmuir was selected to analyze the equilibrium data of cadmium sorption onto the composites.²⁰

The amount of cadmium sorbed (q (mg g⁻¹)) was calculated by the following expression:

\[ q_e = \frac{(C_0 - C_e)V}{1000 m} \]

where \( q_e \) is the sorption capacity in mg g⁻¹, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of Cd in mg L⁻¹, \( V \) is the volume of the solution in mL and \( m \) is the weight of the sorbent (MII, MNI) expressed in g.

2.4.3. Analytical procedure for Cd(II) determination in the magnetic flow-through minicolumn (MC) system. The pre-concentration system is shown in Fig. 2. The MC was constructed from an acrylic cylinder (3.0 cm long, 1.6 cm in diameter). The inner part was drilled to obtain inner
dimensions equal to 10 mm in length and 0.5 mm i.d. One circular neodymium permanent magnet (outer diameter: 28 mm; inner diameter: 23 mm; height: 18 mm) was set around the MC as shown in Fig. 2.

The MC was slurry loaded with the solids (0.010 g) one at a time, by a peristaltic pump at a flow rate of 1.0 mL min\(^{-1}\) and used for 800 enrichment cycles before repacking.

In a typical experimental procedure under optimized conditions, 10 mL of the sample was introduced in the MC filled with MII or MNI at a flow rate of 2.0 mL min\(^{-1}\) for MII and 1.5 mL min\(^{-1}\) for MNI. 50 µL for MII and 200 µL for MNI of 1.0 M HCl were employed for elution at a flow rate of 0.5 mL min\(^{-1}\). An aliquot of 20 µL was injected into the graphite furnace and the analytical signal was obtained.

Prior to a new cycle of preconcentration–elution, the fillers in the minicolumns were rinsed with 0.5 mL of DDW to remove the residual eluent.

### 3. Results and discussion

#### 3.1. Characterization of Fe\(_3\)O\(_4\) MNI and MII sorbents

**3.1.1 Magnetic property analysis.** The magnetization of Fe\(_3\)O\(_4\), MNI and MII samples is shown in Fig. 3(A). The Fe\(_3\)O\(_4\), MNI and MII achieved a saturation magnetization value of 62.61, 61.74 and 59.13 emu g\(^{-1}\), respectively. The decrease of saturation magnetic intensity indicates that the magnetic particles are coated.\(^{25,44}\) As there is no hysteresis loop and coercivity is close to zero, the superparamagnetic properties of Fe\(_3\)O\(_4\) nanoparticles were maintained.\(^{25,44}\) The presence of superparamagnetism in MII and MNI enables the use of an external magnetic force for the purposes described below (see the inset in Fig. 3(A)).

**3.1.2. DRX.** The results (Fig. S1) show that the diffraction peaks of Fe\(_3\)O\(_4\) match well with the database of magnetite. All peaks of MII and MNI are almost the same as those of Fe\(_3\)O\(_4\) with a slight decrease in intensity. Nonetheless, the crystalline structure of the magnetite is essentially maintained.\(^{25,41}\)

**3.1.3. FT-IR spectra.** Fig. 3(B) shows the FTIR spectra of Fe\(_3\)O\(_4\), MNI and MII. The bands at 632 cm\(^{-1}\) and 563 cm\(^{-1}\) corresponding to the stretching of Fe--O were observed in all spectra. This indicates that the Fe\(_3\)O\(_4\) particles were encapsulated inside the MNI and MII solids. The presence of the coating was verified by the absorption bands observed in the MNI and MII spectra at 3450, 1100 and 950 cm\(^{-1}\), which correspond respectively to the stretching, asymmetric stretching and bending of Si–OH on the surface. On the other hand, N–H stretching (3200–3500 cm\(^{-1}\)) and C–N stretching (1030–1230 cm\(^{-1}\)) overlap with the broad absorption band of the silanol group, the Si–O–Si vibrations and OH vibration.\(^{44}\) Also, a very weak N–H stretching peak can be seen at 1490 cm\(^{-1}\) for MNI and MII assigned to the NH\(_2\) deformation modes of the amine groups. In addition, the weak band in the region of 2850–2950 cm\(^{-1}\) is ascribed to the asymmetric vibration of C–H groups.\(^{44}\) These results indicate the successful incorporation of amino groups in the structure of both MNI and MII solids.\(^{25}\)

**3.1.4 SEM images.** From the analysis of the SEM images of the Fe\(_3\)O\(_4\), MNI and MII samples, an average particle diameter of (11 ± 2) nm was obtained for the magnetite nanoparticles and (13 ± 2) nm and (15 ± 2) nm for MNI and MII respectively (Fig. S2). This increase in the diameter of the synthesized solids with respect to that of Fe\(_3\)O\(_4\) confirms the presence of the organosilane coating. Similar values of particle size and coating have been found in the literature.\(^{25,45}\)

#### 3.2. Effect of the pH

Almost 100% adsorption was obtained for pH values between 6 and 8, and pH = 7 was selected for further experiments.

Fig. 4(A) shows the effect of pH on the adsorption of Cd(II) on MII and MNI. For both solids, adsorption is negligible at very low pH which is consistent with the protonation of amine groups at the surface. As pH increases, adsorption increases mainly due to a combined effect of adsorption, electrostatic attraction (note the negative surface of silanol groups) and chelation via the deprotonation of the amino groups.\(^{25,34}\)

**3.3. Kinetics studies**

Based on the knowledge that the time of analyte/filler contact is of great relevance at the moment of preconcentration in a flow system, we studied the kinetic adsorption behavior of both solids towards Cd(II). As shown in Fig. 4(B) Cd(II) retention at optimal pH increases with time, reaching the equilibrium value at 10 min for MNI and 5 min for MII. The behaviors of both solids are basically in line with those of common imprinted mesoporous silica as reported elsewhere.\(^{25,26,34}\)

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**Fig. 3** (A) Magnetization curves. Inset picture: MII and MNI suspended in DDW (on top) and separated by an external magnet (bottom). (B) FTIR spectra.

**Fig. 4** (A) Effect of pH on the adsorption of Cd(II) and (B) adsorption kinetics for MNI and MII.
In order to investigate the rate-limiting steps involved in the processes of adsorption of Cd(II) ions onto MNI and MII sorbents, the pseudo-first (PO1) and pseudo-second order (PO2) kinetic models were used. Results in Table 1, for the non-linear fit, showed PO2 to be the best-fitting model. Based on the PO2 model, the rate-limiting step could be chemisorption.

### 3.4. Adsorption capacity

The results of adsorption capacities of Cd ions on the sorbents were fitted by Langmuir and Freundlich isotherms. The fitting plots in Fig. 5(A) and (B) show that the Langmuir adsorption model could explain the adsorption behaviour of Cd(II) on both materials. So, it could be considered that a monolayer coverage of analytes is formed at the surface of the sorbent. Non-linear regression fittings were employed to calculate the maximum adsorption capacity of Cd ions on the two sorbents, which was found to be 49 mg g⁻¹ for MNI and 136 mg g⁻¹ for MII. The greater adsorption capacity of Cd(II) on MII compared to MNI is in agreement with other results reported in the literature, and the main reason for this difference could be attributed to the imprinted cavities for Cd(II) present in MII. Moreover, the values obtained were higher than those reported using similar syntheses for Cd(II).

### 3.5. Experimental set-up of the MC flow-through system

The homogeneous distribution of the magnetic sorbent is a key factor in the design of flow-through systems with MC. In addition, either the bleeding or the particle aggregation of the filler inside the MC needs to be prevented in order to avoid loss of material or obstructions to the free movement of the fluids. These attributes are of paramount relevance at the moment of optimization of the main figures of merit as presented below. In this regard, different arrangements including the use of one or two rectangular permanent magnets perpendicular to the MC have been reported in the literature, whilst the use of a single circular permanent magnet has not been reported up to now. In the case of perpendicularly placed magnets, adhesion is reported to be observed only on those walls with which the magnets are in contact.

However, the arrangement with a circular magnet around the MC results in a uniform distribution on all walls of the MC with a hole in the center, which is advantageous in systems such as ours where a small amount of filler material is allowed (see Fig. 6(A) and (B)). The adhesion of the solid to the walls of the MC was also tested up to the highest flow rates allowed by the peristaltic pump. No loss of material was observed. It is important to mention that the chemical and flow characteristics of the packed MC remained unchanged for more than 800 analytical cycles, so it was not necessary to refill the MC with sorbent at any point during the work. For more details on the experimental setup, see the ESI.

### 3.6. Optimization of dynamic conditions for MC MSPE

Dynamic SPE conditions for retention and quantitative release of Cd(II) in an MC filled with MNI or MII were optimized by applying the one variable at a time (OVAT) method. For this, the loaded mass of Cd(II) was kept constant and equal to 10 mL of 0.02 ng mL⁻¹ Cd(II) at pH 7. The same was true for the amount of each filler which was kept equal to 0.010 g.

#### Table 1  Kinetic adsorption parameters calculated using pseudo-first-order and pseudo-second-order models for both filling materials. Concentration of Cd(II) = 5 mg L⁻¹; Cd(II) volume = 10 mL; sorbent dosage = 0.010 g

<table>
<thead>
<tr>
<th>Filling</th>
<th>Pseudo-first-order (PO1)</th>
<th>Pseudo-second-order (PO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{e1}^a$ (mg g⁻¹)</td>
<td>$K_1^b$ (min⁻¹)</td>
</tr>
<tr>
<td>MNI</td>
<td>3.58</td>
<td>0.381</td>
</tr>
<tr>
<td>MII</td>
<td>4.03</td>
<td>0.437</td>
</tr>
</tbody>
</table>

$^a q_{e1}$ = sorption capacity for PO1.  $^b K_1$ = Kinetic constant for PO1.  $^c q_{e2}$ = sorption capacity for PO2; constant for PO1.  $^d K_2$ = Kinetic constant for PO2.
First, the type and concentration of the eluents were assayed. Since Cd(II) was not retained in acid media (see the batch experiments in Section 3.2), HCl and HNO₃ could be a good choice for elution. HNO₃ is an oxidant and so, HCl was preferred in order to prevent oxidation of the amine groups of the fillers. Moreover, it is a more suitable choice for GFAAS operation. HCl concentration was changed between 0.1 and 1.5 M, keeping both sample and eluent flow rates constant and equal to 1 mL min⁻¹. Fig. 7(A) shows that from 1.0 M HCl onwards, the analyte is completely recovered. Thus, 1.0 M HCl was chosen for further experiments.

Sample and elution flow rates were optimized one at a time. Flow rates were changed between 0.5 and 5.0 mL min⁻¹, values compatible with the proper operation of the peristaltic pump. Here lies one of the principal characteristics of the experimental setup (see Fig. 1): since the filler remains attached to the walls of the MC, the maximum flow rate can be used with no holder frits, preventing solid bleeding or obstructions to the free movement of solutions as told above.

Fig. 7(B) shows the percent recovery of Cd for both fillers. For MNI, optimal conditions (>98% recovery) were found at a sample flow rate of 1.5 mL min⁻¹ (preconcentration) and an eluant flow rate of 0.5 mL min⁻¹ (analyte release). For MII, 2.0 mL min⁻¹ and 0.5 mL min⁻¹ showed the best performance (>98% recovery). Note that flow values for preconcentration are the result of a compromise situation between the sample throughput and the time of analyte/sorbent contact: higher values increase sample throughput but decrease the time of analyte/sorbent contact and thus the efficiency of retention. Regarding eluant flow rate, any value below 1 mL min⁻¹ showed optimal results. In this case, 0.5 mL min⁻¹ was selected in order to allow the proper operation of the pump (with no pulsation).

In order to improve the preconcentration factor (PCF) while keeping the quantitative recovery of the analyte, different eluant volumes were tested. MII showed a PCF of 200 for a volume of 50 µL of eluant whilst MNI showed a PCF of 50 for 200 µL of eluant (see Fig. S4†).

The effect of sample volume was also assayed. Any value below 50 mL allowed 98% quantitative recovery of the analyte (Fig. S5†). However, 10 mL was chosen in order to optimize the sample throughput. So, 10 mL of sample was employed for further experiments.

As mentioned above, under these optimal conditions the PCF was four times higher for MII. These results can be correlated with the arrangement of the ligand groups in the imprinted materials. MII provides specific cavities able to efficiently coordinate the target analytes (Cd ions in our case). Furthermore, this should be reflected in an increase in selectivity when other ions are also present in the samples under analysis.

3.7. Selectivity experiments and interference studies

To compare the selectivity of MII and MNI with respect to Cd(II), the maximum tolerable level (MTL) of a given interferent was studied. For this, a study of the cationic and anionic interferents of usual occurrence in natural waters was carried out. MTL was defined as the maximum concentration of the interferent that allows a theoretical recovery of the analyte (Cd(II) in this case) no lower than 98%.

To this end, 10 mL solutions containing 0.02 ng mL⁻¹ Cd(II) were added with increasing amounts of co-existing ions one at a time, and treated according to the optimal conditions described above. Results are shown in Table 2.

As expected, MII shows a better selectivity for Cd(II) than MNI, which is most clearly revealed as the ratio between MTLs which ranges between 100 and 300 depending on the co-existing ions. In the case of cations one of the possible factors of this behavior is the inherent selectivity of the amino-functionalized group. Since the amino group is a soft base, it would not interact with alkaline and alkaline earth metals, which are classified as hard acids. On the other hand, Pb(II), Zn(II), Ni(II) and Co(II), which have an identical charge and are similar in size to Cd(II), are borderline acids while Cd(II) is a mild acid so it forms more stable chelates.⁶⁶

Added to these are two other factors due to the Cd(II)-II coordination geometry and cavity or hole size of the impressed ion. In the case of coordination geometry, II can provide an arrangement of the chelating amino group that is more suitable for the coordination of the Cd(II) ion than the NI.⁴⁷,⁴⁸

3.8. Analytical performance

Under the optimal conditions, calibration curves ranging between 2.5 and 100 ng L⁻¹ Cd were obtained for MNI and MII.

Table 2 Maximum tolerable level (MTL) of interferents in the determination of 0.02 ng mL⁻¹ Cd(II) for MNI and MII fillings under optimized conditions. In all the cases the recuperation of Cd(ii) was greater than 98%

<table>
<thead>
<tr>
<th>Ion</th>
<th>MNI MTL (ng mL⁻¹)</th>
<th>MII MTL (ng mL⁻¹)</th>
<th>MII/MNI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>200</td>
<td>35 000</td>
<td>175</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>35</td>
<td>3500</td>
<td>100</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>50</td>
<td>7500</td>
<td>150</td>
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<tr>
<td>Co(II)</td>
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<td>7500</td>
<td>150</td>
</tr>
<tr>
<td>Na(I)</td>
<td>2000</td>
<td>60 000</td>
<td>300</td>
</tr>
<tr>
<td>Cl⁻</td>
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<td>13 000</td>
<td>130</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>700</td>
<td>90 000</td>
<td>129</td>
</tr>
</tbody>
</table>

a MTL MII/MTL MNI.

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Fig. 7 (A) Percent recovery for different HCl concentrations for both fillers. Sample volume: 10 mL of [Cd(II)]: 0.02 ng mL⁻¹, sample flow rate: 1 mL min⁻¹, elution flow rate: 1 mL min⁻¹, and eluent volume: 1 mL. (B) Effect of the sample flow rate on the preconcentration of Cd by passing through 10 mL of 0.02 ng mL⁻¹ Cd(II) at pH = 7.
Six replicates were measured for each standard and a linear regression equation $A = 0.01218[\text{Cd(II)}] + 0.0052$ ($R^2 = 0.9998$) for MII and $A = 0.00784[\text{Cd(II)}] + 0.0052$ ($R^2 = 0.9995$) for MNI were obtained (see Fig. S6†).

The results showed an increment in sensitivity of 1.55 for MII when compared to MNI. Moreover, the limit of detection (LOD) (defined as LOD = 3Sb/m, where Sb is the standard deviation of ten replicates of the blank and m is the slope of the calibration curve after preconcentration) was 0.99 ng L$^{-1}$ Cd with RSD% = 2.5% ($n = 7; 20$ ng L$^{-1}$ Cd) for NI whereas for II it was 0.63 ng L$^{-1}$ Cd with RSD% = 2.0% ($n = 7; 20$ ng L$^{-1}$ Cd).

These results are consistent with the PCF calculated below and show the analytical advantage of ion imprinting in filler materials. In order to evaluate the reusability and stability, successive preconcentration-elution cycles were studied. The results showed no significant loss in analytical sensitivity (no changes in the slope of the calibration curve) for more than 800 cycles for both fillers.

A comparison of the developed method with other solid-phase-GFAAS methods for Cd(II) is provided in Table 3.

Note that all the methods selected for comparative purposes have employed GFAAS to record the analytical signal. In this way, the optimization of the analytical performance reveals the efficiency of the pretreatment and not that of the detector.

As shown in Table 3, most of the parameters are similar or even lower than those previously reported. In addition, other advantages include: elimination of the need for matrix modifiers$^{29}$ for GFAAS operation; lower sample and reagent consumption; high sample throughput; and longer lifetimes expressed in terms of the number of sorption/desorption cycles.

### 3.9. Applications in real samples

The developed method was applied to the determination of Cd(II) in tap water and osmosis water samples.

After filtering with 0.45 mm cellulose filter membranes, the Cd(II) content in real water samples was determined by spiking. As is summarized in Table 4, the recoveries of Cd(II) were between 98.0 and 101.7% (RSDs = 2.0–3.5%, $n = 3$), which were found to be satisfactory, confirming the reliability of the method for analysis of real samples.

For comparison, ICP-MS was employed. For both tap water and osmosis water the results were below the ICP limit of detection of 50 ng L$^{-1}$, except in the case of the tap and osmosis water with 50 ng L$^{-1}$ Cd(II) added (see Table 4).

### 4. Conclusions

For the first time, a magnetic material with ion imprinting (MII) has been successfully used in a flow-through system holding an MC packed with MII for the determination of microamounts of Cd(II).

A simple and novel setup using only one permanent magnet applied around the MC allowed homogeneous immobilization of the solid on the walls.

The joint effect of ion imprinting (increase of selectivity) and magnetism (more operational freedom) rendered an improved analytical performance under dynamic conditions.
The design of the flow-through system minimizes manual handling, the risk of contamination and loss of sorbents, and allows high throughput analysis.

Moreover, this new method has significant advantages over other MSPE approaches using GFAAS detection: no toxic organic solvents required; low sample and reagent consumption; low waste; high sample throughput; improved figures of merit; and excellent reusability.

Both the imprinted and unimprinted synthesized magnetic materials were coated by the simple and fast one-step sol–gel process using ethanol and water as solvents, resulting in an environmentally friendly approach that complies with some of the postulates of green chemistry.

Future work will be aimed at extending the application of the developed method to the speciation of other trace/ultratrace ions of ecotoxicological interest.

Conflicts of interest
The authors declare no conflicts of interest in this article.

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