



Silver nanoparticle-cellulose composite for thin-film microextraction of Cd and Pb as dithiocarbamate derivatives followed by inductively-coupled plasma mass spectrometry determination

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ABSTRACT

Preconcentration of Cd and Pb at ultratrace level in waters following filtration through silver nanoparticles-cellulose composites used for thin-film microextraction was performed. The new procedure was based on the formation of pyrrolidine dithiocarbamate (APDC) derivatives, which showed a large affinity toward the AgNPs. For this purpose, cellulose filters modified with AgNPs were prepared *in situ* upon reduction of silver ions by sodium tetrahydroborate. The effect of several experimental parameters such as the kind of derivatization agent and its concentration, sample pH, desorption conditions and volume of filtered sample was assessed. Cd and Pb were quantitated in the eluates by inductively coupled plasma-mass spectrometry (ICP-MS). Filters were characterized by scanning electron microscopy (SEM) in backscattering electron mode and combined with energy dispersive X-ray spectrometry, showing the presence of Ag and S in the cellulose filter. The repeatability expressed as relative standard deviation (RSD,%) was 1.4% for Cd and 5.8% for Pb. Methodological detection limits were 0.6 and 8.5 ng/L for Cd and Pb, respectively. The method was applied to several environmental waters.

1. Introduction

Trace elements are typically referred to those elements present at minute concentration in the environment, some of them posing a threat to life even at very low concentration due their high toxicity, persistence and ability to accumulate [1]. Thus, heavy metals such as Cd and Pb require the use of very sensitive analytical techniques such as electrothermal-atomic absorption spectrometry (ETAAS) [2], inductively-coupled plasma mass spectrometry (ICP-MS) [3], anodic stripping voltammetry (ASV) [4], inductively-coupled plasma optical emission spectrometry (ICP-OES) [5] and total reflection X-ray fluorescence spectrometry (TXRF) [6] so as to meet the low concentration levels found in most environmental and biological samples. Thus, the maximum contaminant levels recommended in drinking water for Cd were 3 ppb according to the World Health Organization (WHO) [7] and 5 ppb according to the United States Environmental Protection Agency (USEPA) [8] and European Commission (EC) [9]. For Pb, these values were 10 ppb according to WHO [7] and EC (it should be 5 ppb in 2036) [9] and 15 ppb according to USEPA [8].

ICP-MS is a hybrid technique providing very low detection limits along with wide linear range and multielemental capability [10,11]. In order to push the detection limits even further for harmful ele-

ments, preconcentration strategies are typically developed prior to detection [12,13]. However, this step may lengthen the analysis time, it may involve several complex and tedious operations and more importantly, there could be contamination risks giving rise to bias [13]. In recent years, modern preconcentration approaches have evolved toward a miniaturization of devices, providing significant enrichment factors with minimal volume of reagents, eluents and samples [14]. Among them, solid-phase extraction (SPE) [15] as well as its miniaturized version (solid-phase microextraction, SPME) and derived modes have found much success for preconcentration of trace elements [12,16]. SPME operates at equilibrium conditions with a very low volume of extractant phase as coating applied to a fiber which results in low extraction efficiency. Solid-phase microextraction using a sorbent spread in the form of a thin film (*i.e.* thin-film microextraction, TFME), introduced for the first time by Pawliszyn in 2003 [17], is particularly attractive since the surface-to-volume ratio of the sorbent is larger, thus enhancing the extraction efficiency [18]. When supporting the sorbent onto a porous membrane, a dynamic extraction approach can be outlined, which allows achieving enhanced extraction efficiency along with low sorption/desorption times.

Cellulose-based materials have found interesting applications in different steps of analytical processes, such as sample preparation (clean-

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up and preconcentration), chromatography separations, capillary electrophoresis and microfluidic devices [19]. Cellulose is the most abundant biopolymer in nature, possessing high porosity, biodegradability and ease of surface modification [20,21]. Cellulose membranes (CM) acting as preconcentration platforms have been widely used as a simple, fast and efficient approach for preconcentration of trace elements after derivatization to yield hydrophobic species that can be retained by the filter (e.g. neutral chelates or ion-pairs) following filtration of the sample solution [22]. In these methods, sorbents are added to the sample solution or immobilized onto the cellulose filter. Analytical determinations are accomplished after direct analysis of the filter by X-ray fluorescence spectrometry (XRF) [23,24] or ETAAS [25], dissolution in organic solvents like N,N-dimethylformamide (DMF) prior to UV-vis spectrophotometry [26], digestion by mineral acids at high temperature followed by flame atomic absorption spectrometry (FAAS) [27–29], ICP-OES [30] or ETAAS [31], dissolution with tetramethylammonium hydroxide and ETAAS [32] or after metal desorption from filters with diluted HNO₃ and FAAS [33,34].

Given the enhanced sorption ability displayed by nanomaterials, these have been used for modification of the cellulose surface [21,35,36] so as to extend the applicability of this biopolymer for preconcentration. Thus, cellulose membranes modified with graphene oxide [37] and graphene oxide/carbon nanotubes (GO/CNTs) [38] have been applied to the preconcentration of several metal ions prior to analysis by TXRF. Silver nanoparticles (AgNPs)-cellulose composites have found interesting applications as cellulosic antibacterial materials in food packaging, catalysis, environmental protection, health care, etc. [39].

In earlier papers by our group, we have shown the feasibility of using cellulose filters modified with AgNPs for preconcentration of volatile hydride-forming elements [40] as well as for direct preconcentration of Hg(II) in waters following a simple filtration approach [41]. In this work, the method is extended for preconcentration of Pb(II) and Cd(II) following their conversion into pyrrolidindithiocarbamate derivatives, filtration through cellulose membranes modified with AgNPs and ICP-MS analysis.

2. Experimental

2.1. Apparatus

An inductively-coupled plasma mass spectrometer (ICP-MS) X Series ICP-MS (Thermo Elemental, Thermo Fisher Scientific, Bremen, Germany) was employed for simultaneous element quantification. For the characterization of cellulose substrates, the scanning electron microscope JEOL JSM 6700 (Japan Electron Optics Laboratory Co. Ltd., Mitaka, Tokyo, Japan) was used in backscattering electron mode (BSE) and combined with energy dispersive X-ray spectrometry (EDS). A cup-horn sonoreactor UTR200 (200 W, 24 KHz) (Dr.Hielscher, Tltow, Germany) was used to facilitate the desorption of analytes from the cellulose filters. A Millipore Sigma Simplicity ultrapure water system (Millipore Iberian S.A., Madrid, Spain) was utilized for obtaining high-purity deionized water.

2.2. Reagents and materials

Analytical grade reagents were utilized throughout this work. Filter paper 602 H (Whatman, Germany) were used for the preparation of modified Ag cellulose filters.

HNO₃ 65% m/m (Prolabo), NaOH (Sigma-Aldrich) and H₂O₂ 30% m/m (Panreac) were employed for different operations (i.e. pH adjustment, filter digestion, etc.). NaBH₄ 96% m/m (Merck), AgNO₃ (Scharlau, Barcelona, Spain), and ethanol (VWR, Fontenay-sous Bois, France), were employed for the *in situ* synthesis of Ag nanoparticles. Ammonium pyrrolidine dithiocarbamate (APDC) (Fluka, Buchs, Switzerland), sodium diethyldithiocarbamate (DDTC) (Merck), ethylenediaminetetraacetic acid (disodium salt) (EDTA) (VWR, BDH Prolabo, Leicester-

shire, England) were tested as complexing agents. Stock standard solutions containing 1000 mg/L of Cd and Pb were used (Panreac) for method optimization. An ICP Multi Element Standard Certipur® VI (Merck) (SPC Science Québec, Canada) was used for calibration in ICP-MS. QC-1038 *Trace metals (Dissolved)*-1 and QC-1187 *Trace Metals-ICP Sample 1* (Sigma-Aldrich) were used for method validation. In addition, two simulated water samples mimicking the major composition of spring water and groundwater and a synthetic urine sample were fortified with Cd and Pb and analyzed by the proposed method.

2.3. Procedure for NPs synthesis onto cellulose filters

The preparation of cellulose filters modified with AgNPs was based on the reduction of silver ions by sodium tetrahydroborate as indicated elsewhere [41]. Briefly, 25 sheets of filter paper of 10 mm diameter were successively immersed in AgNO₃ (25 mL; 0.02 M; 3 min), ethanol (25 mL; 1 min), NaBH₄ (25 mL; 0.01 M; 5 min) and water (25 mL; 1 min). Finally, filters were air-dried in a laminar flow hood before use. The filter paper changes from white to yellow color during the synthesis. After washing with ethanol, filters were immersed in NaBH₄, rinsed with ultrapure water and air-dried.

2.4. Preconcentration, desorption and measurement procedures

The preconcentration procedure consisted of vacuum filtration of aqueous (standard or sample) solution (50 mL) adjusted at pH=3 and containing APDC (5 mg) in solution through a filter paper of 10 mm Ø modified with AgNPs. A standard solution containing 50 µg/L of Cd(II) and Pb(II) was employed for optimization purposes. 5 mg of APDC were added and the resulting solution was stirred for 5 min at room temperature to facilitate the dissolution of APDC and the formation of neutral chelates. After vacuum filtration, the cellulose filter was inserted in an Eppendorf vial and metal desorption was performed by adding 1 mL of 3 M HNO₃, followed by sonication in a cup-horn sonoreactor for 5 min at 60% amplitude.

Digestion of filters was performed with 1 mL of concentrated HNO₃ and 1 mL of commercial H₂O₂ in 15 mL falcon® tubes heated at 80 °C for 24 h.

For ICP-MS determination, instrumental stability and tuning was checked using a solution of 10 µg/L of Li, Be, Bi, Ce, Co, In, Pb and U in HNO₃ (2% v/v). Internal standardization was performed using ¹⁰³Rh for ¹¹¹Cd, and ¹⁵⁹Tb for ²⁰⁷Pb. The quantification of Ag (isotope ¹⁰⁷Ag) was performed in a semiquantitative way in order to estimate the amount of Ag released during desorption steps. Instrumental ICP-MS conditions are shown in Table 1. Sample preparation for electron microscopy was made as indicated elsewhere [41].

3. Results and discussion

3.1. Preliminary experiments

Firstly, 50 mL of multielemental solutions of 50 µg/L of Cd(II) and Pb(II) prepared at three different pH (pH=3, pH=6 and pH=8) were filtered through cellulose filters modified with AgNPs. Desorption was performed with 1 mL of 1 M HNO₃ or HCl upon application of ultrasound. No preconcentration occurred due to inefficient sorption of both metal ions onto the AgNPs (Fig. S1). The use of complexing agents was evaluated in order to improve the retention of the studied elements. APDC is a widely used complexing agent to perform the liquid-liquid extraction of metallic ions. The ability of AgNPs to react with complexing reagents such as APDC has already been remarked [42,43]. Thus, different experiments were undertaken to assess the suitability of APDC for enhancing metal sorption onto AgNPs-cellulose composites (Fig. S2): (i) by using APDC in the sample solution so as to form the neutral chelate before filtration; (ii) by impregnating cellulose filters with APDC before filtration.

Table 1
Instrumental ICP-MS conditions.

Instrument: Thermo Elemental X7 Series ICP-MS	
General parameters	
Torch: Quartz (injector 1.5 mm)	
Nebulizer: Meinhard concentric nebulizer	
Spray chamber temperature: Peltier system at 3°C	
Spray chamber: Quartz impact bead	
Interface: sampler Ni cone and skimmer Ni cone	
Autosampler: Cetac ASX-520	
Plasma characteristics	
Forward power: 1300 W	
Sample flow: 1.0 mL/min	
Cool Ar flow: 13 mL/min	
Auxiliary Ar flow: 0.7 mL/min	
Nebulizer Ar flow: 0.85 mL/min	
Mass spectrometer characteristics	
Scanning mode: Peak hopping	
Channels per mass: 3	
Dwell time: 50 ms	
Sweeps per peak: 25	
Number of replicates: 4	

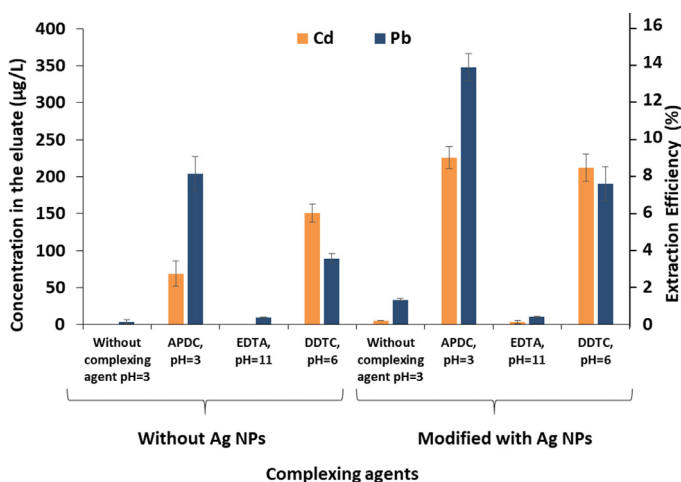


Fig. 1. Filtration using different complexing agents. (A) Experiments with unmodified filters (B) Experiments with filter modified with Ag NPs. Experimental conditions: solution of 50 µg/L at different pH and different complexing agent; 5 min of magnetic stirring; desorption: cup-horn sonoreactor; 5 min; 60% amplitude; 1 mL of 1 M HNO₃.

The use of unmodified filters or the immersion of filters in APDC solution (filters impregnated with APDC) prior to filtration did not provide any preconcentration. However, the addition of APDC to the multielemental standard solution provided improved extraction, especially in the case of filters modified with AgNPs. The amount of Ag in the eluate after desorption varied between 3.7 µg of Ag (without using APDC in the solution) and 0.3 µg of Ag (after filtration in the presence of APDC in the solution or after impregnation of the filter). This could indicate that some stabilization of AgNPs occurs in the presence of APDC resulting in lower desorption of Ag from the filter. Apart from APDC, other complexing agents at different pH were also evaluated in order to facilitate analyte retention, *i.e.* ethylenediaminetetraacetic acid (EDTA) and sodium diethyldithiocarbamate (DDTC). Results are shown in Fig. 1 It can be concluded that the use of APDC and DDTC increased the extraction efficiency of Cd and Pb in AgNPs-modified filters but also in unmodified filters. Similar extraction efficiency were obtained for APDC and DDTC for Cd, yet APDC yielded better extraction for Pb. In addition, DDTC stability at acid pH is lower than that of APDC [44,45], a pH 6 being recommended, *e.g.* [46]. Thus, APDC was selected for further experiments. The initial mass of AgNPs onto filters was estimated following acid digestion with 1 mL of conc. HNO₃ and 1 mL of H₂O₂ at

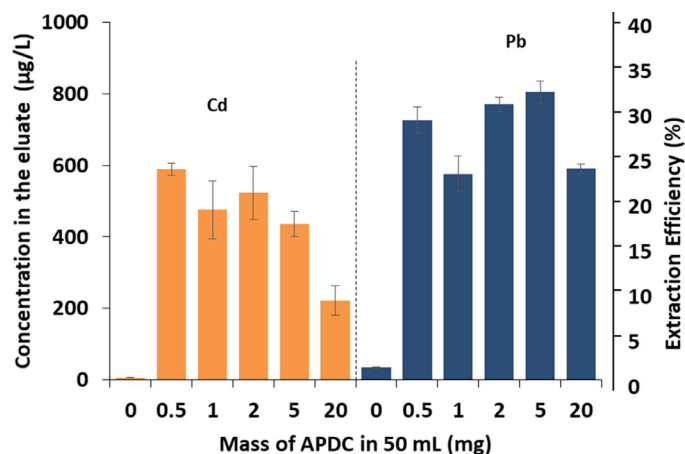


Fig. 2. Effect of the mass of APDC. Experimental conditions: solution of 50 µg/L at pH=3; desorption: cup-horn sonoreactor, 5 min; 60% amplitude; 1 mL of 1 M HNO₃.

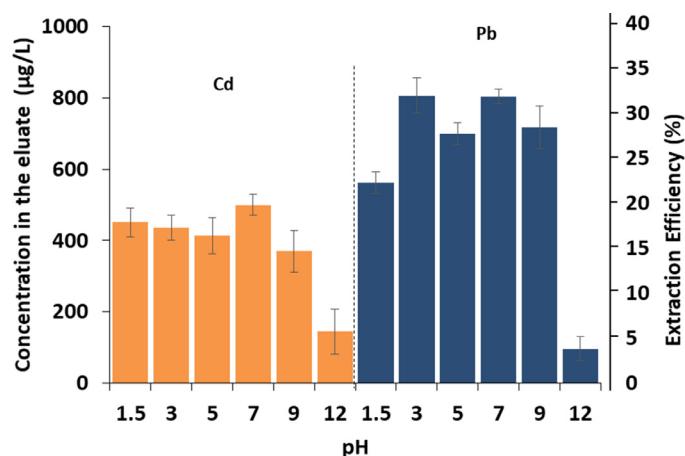


Fig. 3. Effect of the pH of standard solution. Experimental conditions: solution of 50 µg/L with 5 mg APDC; 5 min of magnetic stirring; desorption: cup-horn sonoreactor; 5 min; 60% amplitude; 1 mL of 1 M HNO₃.

80°C as 27.6 ± 7.2 µg. The stability of the AgNPs-cellulose composite subjected to microextraction was also evaluated. The Ag mass found in filters after microextraction was 27.1 ± 0.9 µg when 1 M HNO₃ is used for elution.

3.2. Optimization of the amount of APDC

The mass of APDC in solution was evaluated from 0.5 to 50 mg. After adding APDC, the sample solution was maintained under magnetic stirring for 5 min. Results are shown in Fig. 2. In the case of Pb, a mass of APDC in the range of 0.5–20 mg provided similar results. For Cd, a mass of 20 mg provided a decreased extraction. Moreover, it was observed that the mass of Ag eluted decreased with increasing amount of APDC (0.5 µg of Ag for 10 mg of APDC; 0.2 µg of Ag for 50 mg of APDC), thus reinforcing the hypothesis of the stabilization of AgNPs with APDC.

3.3. Optimization of pH of the sample solution

Since pH is a variable that can influence the complexation reaction and retention on cellulose filter modified with Ag NPs, the effect of pH of the sample solution was assessed. pH was studied from 1.5 to 12 (maintaining constant the mass of APDC at 5 mg), results being shown in Fig. 3. Best results were obtained between pH=3 and pH=7. As expected, at acid pH, APDC was protonated and the formation of com-

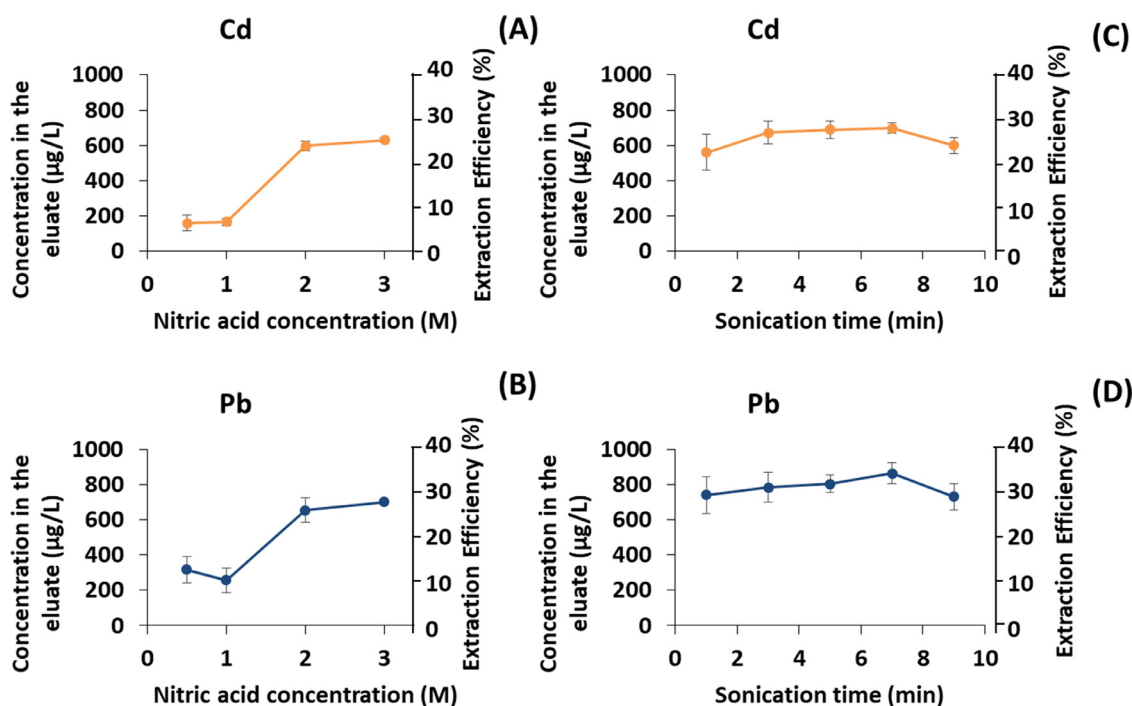


Fig. 4. Effect of desorption conditions. (A, B) Nitric acid concentration. (C, D) Sonication time. (A) and (C) Cd; (B) and (D) Pb. Experimental conditions: solution of 50 µg/L at pH=3 with 5 mg APDC; 5 min of magnetic stirring; desorption: cup-horn sonoreactor; 60% amplitude; 1 mL of acid. (A and B) maintaining the sonication time at 5 min. (C and D) maintaining the nitric acid at 3 M.

plexes with target elements was reduced, whereas at basic pH, these elements were not stable at ultratrace levels. A pH=3 was selected for further experiments.

3.4. Study of desorption conditions

The effect of desorption conditions such as the concentration of HNO₃ and the sonication time was also studied (Fig. 4). Desorption was performed using a HNO₃ concentration between 0.5 M and 3 M. An increase in the extraction efficiency was observed on increasing HNO₃ concentration up to 2 M.

Additionally, the sonication time for desorption was studied in the range of 1–9 min. There was almost no change in the amount of the eluted analytes with increasing sonication time, and therefore, a sonication time as short as 3 min can be used. Instability of the AgNPs-cellulose composite under these desorption conditions (2 or 3 M HNO₃) is observed, which impairs its reuse.

3.5. Effect of the sample volume

The effect of the sample volume was studied by maintaining constant the concentration of analytes (25 µg/L). As can be observed, the obtained concentration of Cd and Pb after filtration increases linearly with the filtered volume up to 100 mL. Therefore, sample volumes at least up to 100 mL could be used without impairing the preconcentration ability of the composite (Fig. 5).

3.6. Characterization of AgNPs-cellulose composites by electron microscopy

The characterization of filters was performed by SEM-BSE and SEM-EDS. AgNPs present a spherical morphology with a particle size in the range of 20–40 nm as shown in the histogram (Fig. 6). SEM-BSE and SEM-EDS images obtained before and after subjecting the filter to microextraction are shown in Fig. 7. The SEM-EDS spectra (Fig. 7C and D) demonstrate that the bright areas in the SEM-BSE images (Fig. 7A and B) correspond to the AgNPs immobilized onto the filter (at 2.984 KeV).

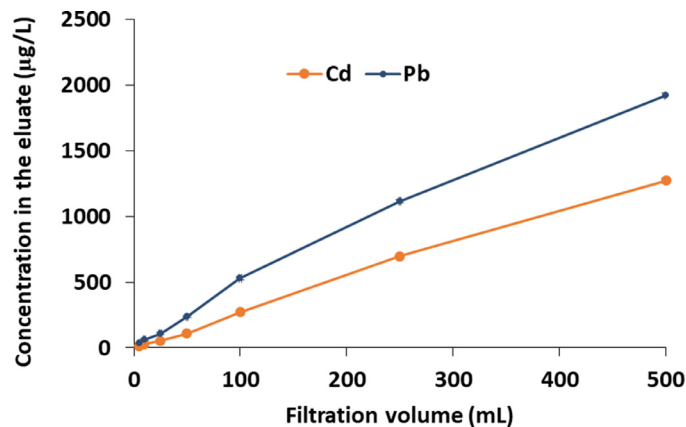


Fig. 5. Effect of sample volume. Experimental conditions: solution of 25 µg/L at pH=3 with 5 mg APDC; 5 min of magnetic stirring; desorption: cup-horn sonoreactor; 5 min; 60% amplitude; 1 mL of 3 M HNO₃. (at constant concentration 25 µg/L).

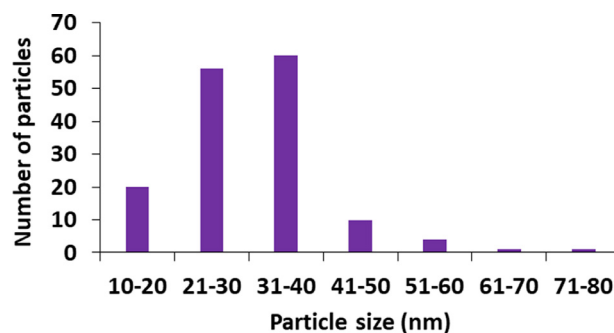


Fig. 6. Size histogram of AgNPs obtained by SEM.

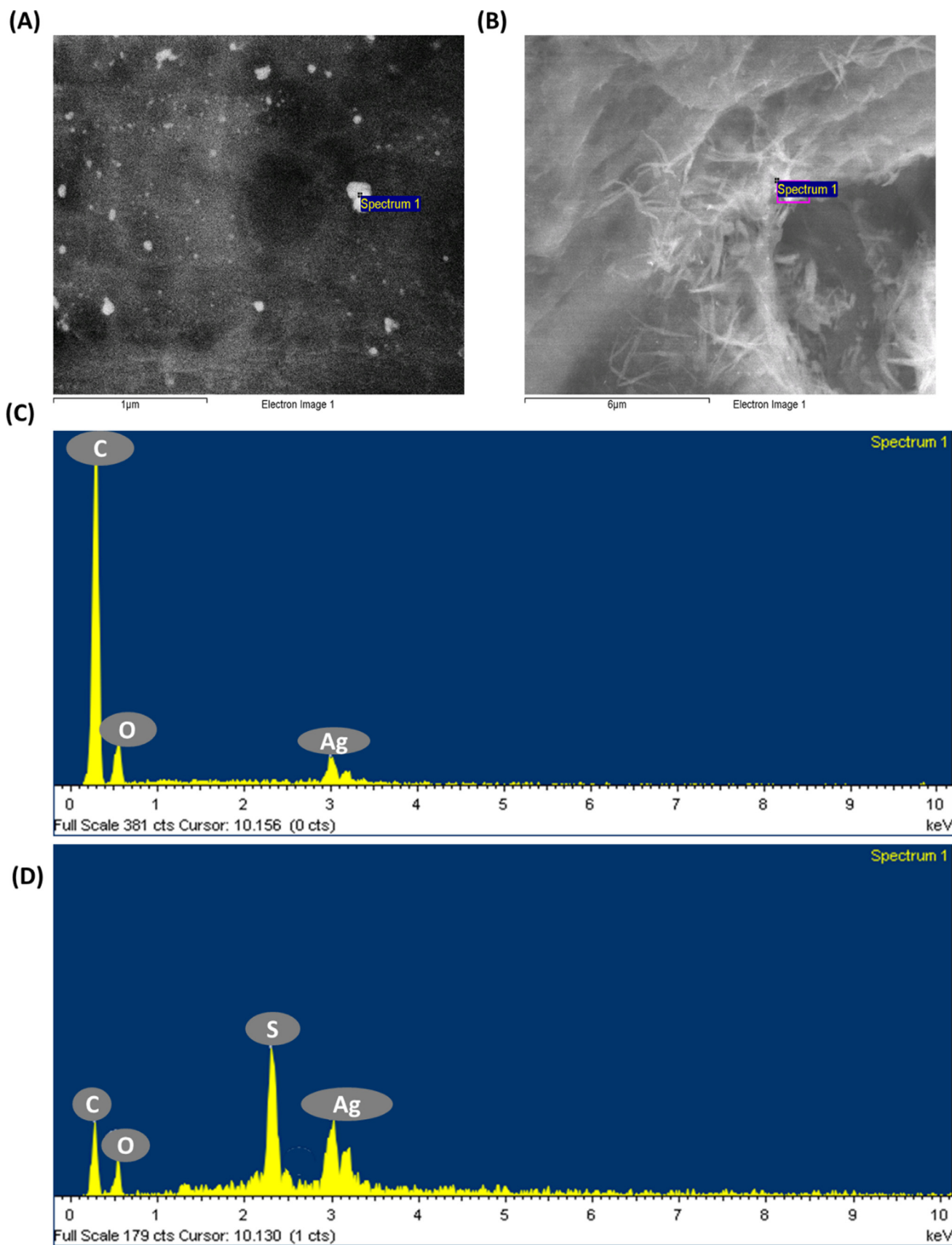


Fig. 7. SEM images. (A) and (B) SEM-BSE. (C) and (D) SEM-EDS. (A) and (C) spectrum obtained for the AgNPs-cellulose composite not submitted to microextraction; (B) and (D) spectrum obtained after subjecting the filter to microextraction (only filtration).

Table 2Analytical results for Pb and Cd in simulated waters and urine samples (mean value \pm standard deviation, $n = 3$).

Synthetic samples	Spiked ($\mu\text{g/L}$) (Cd, Pb)	Cd			Pb		
		Found ($\mu\text{g/L}$)	Recovery,%	RSD,%	Found ($\mu\text{g/L}$)	Recovery,%	RSD,%
Synthetic groundwater ^a	10	10.7 \pm 0.5	107 \pm 5	4.7	10.3 \pm 0.5	103 \pm 5	5
	50	51.8 \pm 1.9	103.5 \pm 3.9	3.7	51.9 \pm 1.0	103.7 \pm 1.9	1.9
Synthetic spring water ^b	10	9.4 \pm 0.4	94.5 \pm 4	4.2	9.07 \pm 0.25	90.7 \pm 2.5	2.8
	50	46.8 \pm 0.8	93.7 \pm 1.5	1.6	42.9 \pm 0.6	85.7 \pm 1.2	1.4
Synthetic urine ^c	10	9.31 \pm 0.22	93.1 \pm 2.2	2.3	9.6 \pm 0.3	95.8 \pm 3	3
	50	46.4 \pm 5.5	92.8 \pm 11	12	48.4 \pm 6.5	101 \pm 13	13

^a 1 mg/L g of humic acid, 1 mg/L of Fe(NO₃)₃ and 0.05 mg/L CuCl₂.^b 25 mg/L NaCl, 25 mg/L CaCl₂, 25 mg/L MgSO₄, 5 mg/L KCl.^c 976 mL HCl 0.02 M, 1.9 mL NH₃ 0.25 M, 14.1 g NaCl, 2.8 g KCl, 17.3 g urea, 0.6 g CaCl₂, 0.43 g MgSO₄.**Table 3**

Analytical results obtained for reference materials.

CRMs	Certified value ($\mu\text{g/L}$) (mean value \pm confidence interval)		Found value ($\mu\text{g/L}$) (mean value \pm deviation standard)		Recovery (%)		t_{calc}	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
QC-1038	443 \pm 4	985 \pm 9	450 \pm 10	92 \pm 96	101.6%	98.7%	$t_{\text{calc}}=1.2$	$t_{\text{calc}}=0.2$
QC-1187	104 \pm 2	72.8 \pm 1.3	103 \pm 6	77.6 \pm 4	99.5%	106.5%	$t_{\text{calc}}=0.1$	$t_{\text{calc}}=2.1$

QC1038 was diluted 1:10 to perform the preconcentration strategy.

 $t_{\text{tab}} = 4.303$ (two freedom degrees; $\alpha=0.05$).**Table 4**

Selected applications for metal preconcentration prior to ICP-MS analysis.

Analytes	Samples	Type of NPs	Preconcentration strategy	LODs	RSDs	Observations	Experimental enrichment factor	Theoretical enrichment factor	Refs.
Cu, Cd and Pb	Daily used water	Nano-clay	SPME-ICP-MS	1300–1.900 ng/L	3.3–5%	Elution with 2 mL of 1 M HNO ₃	34.1	37.5	[52]
Cd, Cr, Ni, Pb and Zn	Natural water and snow	Al ₂ O ₃ impregnated with Alizarin Complexone (minicolumn)	SPE-ICP-MS	–	3.5–7.4%	Elution with 3 mL 0.5 M HNO ₃	16.3	16.7	[53]
Cr, Fe, Cd and Pb	Water matrices	Polymer PPy-CO ₂ sorbent	UAD-SPE-ICP-MS	0.9–5.7 ng/L	2.6–6.2%	Sorption time of 5 min Elution with 1 mL of 2 M HNO ₃ at 0.25 mL/min	13.5	15	[48]
Cd and Pb	Natural water and mussel	CNFs-HOX	SPE-ICP-MS	0.7 - 3.0 ng/L	<5%	Elution with 1.5 mL of 1.2 M HNO ₃	90	100	[49]
Cd, Pb and Zn	Bottled water, tap water, food samples	Amino-functionalized hollow core mesoporous shell silica spheres (NH ₂ -HCMSSs)	SYRINGE-SP-ICP-MS	4–21 ng/L	5.4–7.4%	Elution with 3 M HNO ₃	32.3	33.3	[50]
Cr, Cu, Cd and Pb	Environmental waters and soils	Ti-containing mesoporous silica packed microcolumn	SPE-ICP-MS	7–39 ng/L	6.1- 7.3%	Elution with 0.4 mL 0.1 M HNO ₃ at 1.5 mL/min	10	10	[51]
Cd, Hg and Pb	Environmental waters	Thiol-grafted magnetic polymer	MSPE-ICP-MS	0.2–2.9 ng/L	5.8–10%	Elution with 1 mL containing 0.2 M HNO ₃ and 2% thiourea in 5 min; a permanent magnet is needed.	150	200	[54]
Cd and Pb	Synthetic groundwater, mineral water and urine	Ag NPs immobilized in cellulose (APDC added to aqueous solution)	TFME (filtration)-ICP-MS	0.6 ng/L (Cd) 8.5 ng/L (Pb)	4.7–9.2%	Desorption in 1 mL 2–3 M HNO ₃	16 (Cd) 20 (Pb)	50	This work

APDC, ammonium pyrrolidine dithiocarbamate; CNFs-HOX, carbon nanofibers loaded with 8-hydroxyquinoline; ICP-MS, inductively-coupled plasma mass spectrometry; MNPs, magnetic nanoparticles; MSPE, magnetic solid phase extraction; PPy-CO₂, poly(pyrrole-1-carboxylic acid); SPE, solid-phase extraction; SPME, solid-phase microextraction; TFME, thin-film microextraction; UAD, ultrasound-assisted dispersive.

Both S ($K\alpha$ 2.307 KeV) and Ag ($L\alpha$ 2.984 KeV) [47] were observed in the EDS spectrum corresponding to the filter subjected to microextraction (only filtration process) (Fig. 7D). Therefore, the presence of S due to APDC onto the filter is confirmed, which can be ascribed to the high affinity of S toward Ag and demonstrating that APDC becomes attached to AgNPs (Figs. S3 and S4).

3.7. Analytical figures of merit and validation

Analytical figures of merit included methodological limits of detection (LODs) and quantification (LOQs), preconcentration factors (PF), accuracy and precision (evaluated as repeatability and reproducibility) and linear range. LODs and LOQs were calculated using the 3σ and 10σ criterion, respectively. Methodological LODs were 0.6 and 8.5 ng/L for Cd and Pb, respectively. LOQs were 1.9 and 28 ng/L for Cd and Pb, respectively. Repeatability values ranged were 1.4 and 5.8% for Cd and Pb, respectively, whereas reproducibility values ranged 4.7 and 9.2%. Preconcentration factors of 16 and 20 were achieved for Cd and Pb, respectively. Calibration curves were linear at least up to 100 $\mu\text{g/L}$ for both metals.

Two simulated waters samples (groundwater and spring water) and a synthetic urine sample were spiked with 10 and 50 $\mu\text{g/L}$ of Cd and Pb, and a recovery study was performed (Table 2). The composition of the simulated samples is included at the bottom of the table. A recovery in the range of 86–104% was observed, which demonstrates the absence of matrix effects. Several certified reference materials of aqueous solutions were also analyzed for assessing trueness (Table 3). Satisfactory recoveries (99–107%) were reached for Cd and Pb in both reference materials meaning that no interferent effects are caused by other metal ions present in these samples. No significant differences occurred between the certified and found values when applying a t -test ($\alpha = 0.05$).

3.8. Comparison with other methodologies

Table 4 shows a comparison of the method developed in this work with other recent preconcentration strategies prior to ICP-MS determination, both using sorbents and nanosorbents. The analytical performance of our method is comparable with other SPE preconcentration methods for ICP-MS in relation to LODs [48–51], RSDs [48–53] and enrichment factors [53,50,51]. Nevertheless, our method is less time consuming as compared to others requiring long times for sorbent preparation or sorption operation [52]. Some stages needed to accomplish preconcentration when microcolumns are used, such as introduction of the sorbent phase inside the microcolumn, plugging the column ends and sorbent conditioning, which are time consuming and prone to errors, are also avoided [51]. Some disadvantages of our approach can also be mentioned, *i.e.* non-reusability of the sorbent as this is lost during the desorption process using diluted acid solutions and non-exhaustive extractions owing to the use of microamounts of sorbent and short contact time between the sorbent and sample during the dynamic sorption applied.

4. Conclusions

Thin-film microextraction of Cd and Pb APDC chelates onto AgNPs-cellulose composites was proved to be an efficient, simple and fast preconcentration approach. Metal determination was performed on the acid eluates by ICP-MS. The method allowed enrichment factors of 16 (Cd) and 20 (Pb) with a RSD lower than 6% and limits of detection in the range of ng/L. SEM-EDS spectra show the presence of S in the filter thus demonstrating the affinity of APDC complexes toward AgNPs. Direct analysis of filters for metal determination without elution could be performed directly by techniques such as ETAAS and TXRF, providing a further simplification. Simulated groundwater, spring water and urine synthetic samples provided satisfactory recoveries showing no matrix

interferences. The method was also successfully validated against CRMs of water samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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