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Evaluation of performance of three different hybrid mesoporous solids based on silica for preconcentration purposes in analytical chemistry: From the study of sorption features to the determination of elements of group IB

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ABSTRACT

Several studies involving the physicochemical interaction of three silica based hybrid mesoporous materials with metal ions of the group IB have been performed in order to employ them for preconcentration purposes in the determination of traces of Cu(II), Ag(I) and Au(III). The three solids were obtained from mesoporous silica functionalized with 3-aminopropyl (APS), 3-mercaptopropyl (MPS) and N-[2-aminoethyl]-3-aminopropyl (NN) groups, respectively. Adsorption capacities for Au, Cu and Ag were calculated using Langmuir's isotherm model and then, the optimal values for the retention of each element onto each one of the solids were found. Physicochemical data obtained under thermodynamic equilibrium and under kinetic conditions – imposed by flow through experiments – allowed the design of simple analytical methodologies where the solids were employed as fillings of microcolumns held in continuous systems coupled on-line to an atomic absorption spectrometry. In order to control the interaction between the filling and the analyte at short times (flow through conditions) and thus, its effect on the analytical signal and the presence of interferences, the initial adsorption velocities were calculated using the pseudo second order model. All these experiments allowed the comparison of the solids in terms of their analytical behaviour at the moment of facing the determination of the three elements.

Under optimized conditions mainly given by the features of the filling, the analytical methodologies developed in this work showed excellent performances with limits of detection of 0.14, 0.02 and 0.025 $\mu g\,L^{-1}$ and RSD % values of 3.4, 2.7 and 3.1 for Au, Cu and Ag, respectively.

A full discussion of the main findings on the interaction metal ions/fillings will be provided. The analytical results for the determination of the three metals will be also presented.

1. Introduction

Metals such as gold, silver and copper (Group IB) are often found together in nature and have a great economical importance even though they are difficult to obtain with high purity. However, their multiple applications in jewellery, catalysis, electronics, medicine, etc., have converted their exploitation in a worldwide lucrative activity.

Copper is known as a micronutrient of plants, animals and humans showing low toxicity in comparison to the others. Silver and gold have a much lower natural abundance than copper but, at the same time, a higher toxicity. Mining activities have introduced relatively high concentrations of these metals into the environment [1].

However, the low concentrations found in natural waters limit the employment of direct quantification by atomic absorption spectrometry. Preconcentration steps are generally needed but, they increase the possibility of external contamination and are time and reagent consuming.

In the last few years, hybrid mesoporous solids based on silica have shown remarkable physical and chemical properties that were exploited for different purposes as effluents remediation [2–6], catalysis [7–9] and analytical determinations including solid phase extraction (SPE) [10–15].

The main virtue of a solid for SPE in analytical chemistry is its capacity for the complete and selective retention of the analyte (organic or inorganic). Even though the physicochemical interactions between the analyte and a given solid are the key for its efficient and selective isolation, the literature is mostly dedicated to study the influence of operational and instrumental variables on the analytical performance [5,16–18]. However, these interactions are relevant at the moment of selecting the more suitable filling for a specific compound.

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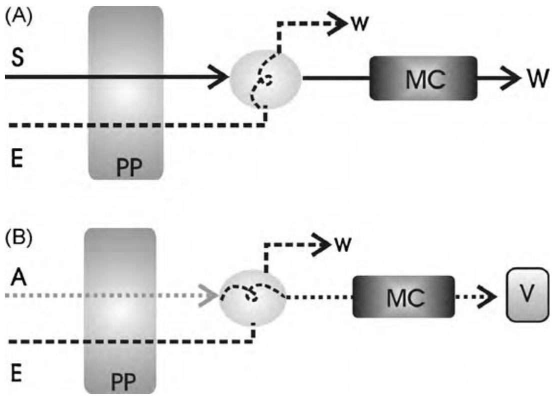

Fig. 1. FI-SPE system. (A) Loading position. MC: Microcolumn, PP: peristaltic pump, E: eluant, S: sample, W: waste. (B) Elution position. A: air, V: vessel.

In previous papers [13,15,19], we have presented kinetics studies on the adsorption of metal ions onto lab-made hybrid mesoporous solids that were specially synthetized in order to obtain the complete and selective extraction of the analyte together with its complete and fast release under flow through conditions at controlled and pre-established pH.

In this work, different silica based organic–inorganic mesoporous solids have been tested for the selective isolation and preconcentration of copper, gold and silver. Decisions were made by considering the interactions of the analytes with three different materials functionalized with 3-aminopropyl (APS), 3-mercaptopropyl (MPS) and N-[2-aminoethyl]-3-aminopropyl (NN) groups under dynamic conditions provided by flow through assemblies. A full discussion on the best option for the determination of each particular metal will be presented in terms of adsorption kinetics behaviour, maximum sorption capacities, easiness of release after retention and analytical performance.

2. Experimental

2.1. Reagents

Standard solutions of Au(III), Ag(I) and Cu(II) were prepared by proper dilution of standard solutions of 1000 mg L^{-1} (Merck Darmstadt, Germany) with double deionized water (DDW) (18 MΩ cm^{-1}, MilliQ Water System, Millipore, Bedford, MA, USA). The pH of the solutions was kept constant through the addition of suitable quantities of HCl or NaOH solutions (Merck) (1 mol L^{-1}).

Sodium tetraethylorthosilicate (TEOS) 98% (Mr = 208.33, d = 0.934 g mL^{-1}), cetyl trimethylammonium bromide (CTAB) (Mr = 364.46), 3-aminopropyltriethoxisilane (APTES) 3-mercaptopropyltriethoxysilane (MPTES) and N-[2-aminoethil]-3-aminopropyltriethoxisilane (Sigma–Aldrich, St Louis, MO, USA) were employed for the synthesis of the organic–inorganic mesoporous solids.

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

2.2. Apparatus

A pH-meter (Boeco BT-500, Germany) with a glass working electrode (Jenway, Essex, England) and a reference electrode of Ag/AgCl (Jenway, Essex, England) was used for pH measurements.

The flow through measurements were performed using a manifold (Fig. 1) assembled with a peristaltic pump (IPC, Ismatec, Glattbrugg-Zürich, Switzerland), 0.5 mm i.d. PTFE® tubings (Cole Parmer, Chicago, IL, USA), and acrylic microcolumns (MC) with their inner part drilled to obtain a 7.9 μL bed volume (10 mm long, 1.0 mm internal diameter). The MC was fixed through 0.25–28 female connectors to the FI tubing, keeping the aspect ratio optimized in order to obtain minimal dispersion together with minimal resistance to the solutions flow. The solids were slurry loaded (0.1 g) into the MC with a plastic syringe and then, two plugs of polystyrene foam were placed at both sides of the MC. Samples were analyzed by electrothermal atomic absorption spectrometry (ET AAS) (Shimadzu AA6800, Kyoto, Japan) equipped with an autosampler Shimadzu ASC-6100. Copper, gold and silver hollow cathode lamps (Hamamatsu, Japan), deuterium lamp background correction and pyrolitic graphite furnaces (platform atomization) were employed throughout the measurements. Temperature programs for all the analytes were utilized according to those provided by the manufacturer.

2.3. Procedure

2.3.1. Synthesis of the mesoporous solids

The solid APS and NN were prepared according to the methodology described by Fowler et al. [20] and previously reported elsewhere [13]. MPS solids were prepared accordingly to Walcarius and Delacôte [21]. Here 2.4 g of CTAB were dissolved in 50 mL of DDW and 45 mL of absolute ethanol (Merck). Then, 13 mL of concentrated ammonia (Merck) were added in order to increase pH and catalyse the hydrolysis of silanes. Afterwards, MPTES and TEOS were mixed in different proportions giving raise to four different mixtures in molar to molar percentages MPTES/TEOS: 5% (m/m), 10% (m/m), 15% (m/m) and 20% (m/m). Each mixture was treated as follows. First, it was added to the CTAB solution slowly and under continuous agitation. Then, it was agitated during 2 h at 25 °C. The obtained solid was filtrated and washed several times with DDW and ethanol and then, it was dried in a vacuum desiccator during 10 h at 100 °C. For the surfactant extraction, the solid was refluxed with HCl 1 mol L^{-1} in ethanol at 75 °C for 24 h. Finally, it was washed again with ethanol and DIW and dried in the vacuum desiccator for 10 h at 100 °C. The percentage of functionalization of the obtained materials was obtained by elemental analysis of nitrogen and sulphur. Amongst the obtained solids; those with 20% (m/m) proportion were selected for analytical purposes.

2.3.2. Adsorption kinetic studies of Cu(II), Ag(I) and Au(III)

Batch experiments were performed by suspending 500 mL of solutions 5 mg L^{-1} of each metal in 100 mg of APS, MPS and NN solids, respectively. Measurements were carried out by taking 100 μL aliquots of the supernatant at different times of contact between the analyte and the filling.

Results were modelled with Langmuir (L), pseudo first order (PO1), pseudo second order (PO2) and double exponential (DE) models, accordingly to Chiron et al. [22].

2.3.3. Optimization of pH for Ag(I), Cu(II) and Au(III) onto the solids

Several batch experiments were conducted with the aim of evaluating the influence of pH on the sorption of the metallic ions onto APS, MPS and NN solids. HCl, NH_3 or NaOH solutions were employed for pH conditioning. For doing this, 5 mL of 500 μg L^{-1} solutions of each metal ion were contacted in separate vessels with each particular solid (0.050 g) at pH values ranging between 1 and 9. Suspensions were agitated during 24 h and then centrifuged at 3200 rpm. Remaining silver, copper and gold were measured in the supernatant solution by ET AAS. The standard programs recommended by the manufacturer were run in all cases.

Table 1a
Q_{max} values for Cu(II) onto the three solids at different pH ranges.

Cu(II)		
Solid	Maximum adsorption pH	Q_{max} (mmol g^{-1})
APS20%	2–6	0.65
MPS20%	1–2	1.65
NN20%	2	0.39

Table 1b
Q_{max} values for Ag(I) onto the three solids at different pH ranges.

Ag(I)		
Solid	Maximum adsorption pH	Q_{max} (mmol g^{-1})
APS20%	8–10	2.05
MPS20%	3–4	0.13
NN20%	3–4	1.79

2.3.4. Analytical procedure for Cu(II), Ag(I) and Au(III) determinations

The preconcentration system is shown in Fig. 1. All columns were slurry loaded as described before (see Section 2.2) and used for over 300 enrichment cycles before repacking in all cases. The use of the same filling is limited principally due to compactation of the solid during the SPE-FI process, leading to an increment in the internal pressure of the FI system and the lose of sensitivity.

In loading position (Fig. 1a) the sample was introduced in the microcolumn (MC) at the optimized adsorption flow rate whilst the loop was filled with the appropriate eluant (E). In the elution position, once the preconcentration time was elapsed, air (A) was introduced in the MC and then, the rotatory valve was commutated in order to inject a known volume of eluant into the MC. The eluted solution was collected in a vessel (V) and it was finally measured by ET AAS. Experiments for selecting the optimized conditions for sorption and desorption will be described below.

3. Results and discussion

3.1. Physicochemical properties of the solids for metal ions adsorption: pH, adsorption capacities and adsorption kinetics

In order to select the most suitable solid for the determination of each particular analyte, changes on the sorption capacities with pH, maximum adsorption capacity and adsorption kinetics at the optimized pH were evaluated.

3.1.1. pH optimization

Experiments were performed in batch. Then, the maximum sorption capacity (Q_{max}) for each ion onto each particular solid was calculated using Langmuir's model which showed the best correlation with the experimental isotherms (results not shown).

Tables 1a–1c show Q_{max} values for each couple analyte/solid at the optimum pH. Figs. 2–4 show the influence of pH on sorption capacity (q) for the best couple solid–analyte.

Q_{max} values in Tables 1a–1c are in agreement with the kind of interactions expected between each particular solid and the different analytes. In this way, more polarizable metallic ions or soft Lewis acids such Au(III) (Pearson's *Hard–Soft, acid–base* o *HSAB* theory) [23–25] should have a better affinity for soft bases such as 3-mercaptopropyl groups. On the other hand, hard Lewis acids such as Ag(I) and Cu(II) ions should interact more efficiently with hard Lewis bases such as 3-aminopropyl and N-(2-aminoethyl)-3-aminopropyl groups. On this basis, different hybrid mesoporous materials could be synthetized as a function of the characteristics of the analyte to be determined.

Table 1c
Q_{max} values for Au(III) onto the three solids at different pH ranges.

Au(III)		
Solid	Maximum adsorption pH	Q_{max} (mmol g^{-1})
APS20%	8–10	6.71
MPS20%	1–4	3.98
NN20%	8–9	4.28

Fig. 2 shows the influence of pH on the adsorption capacity (q) of Cu(II) onto APS when concentrated ammonia is employed for changing pH. An increase of q with pH is observed when the surface charge changes from zero (pH ≈ 2) to negative values. At pH 3–5 a plateau is reached and then, a steep increment from pH > 5 is observed. Neutral pH onwards, the predominant species are positively charged ammonia complexes of copper (i.e. $Cu(NH_3)_4^{2+}$), which are efficiently retained by the negatively charged surface. The presence of these complexes is evidenced by the light blue colour on the surface of the solid. Two possible mechanisms should explain this fact: (a) simple physisorption of $Cu(NH_3)_4^{2+}$ onto the negatively charged silanol groups of APS20% and/or (b) a substitution of ammonia by 3-aminopropyl groups entering in the coordination sphere of ammonia complexes of Cu(II), resulting in a combined effect of electrostatic and complexometric interactions. Considering the different adsorption behaviour observed when APS 20% (Q_{max} = 6.71 mmol g^{-1}) is compared to non-functionalized mesoporous silica (Q_{max} = 0.09 mmol g^{-1}) at the same pH, the second alternative seems more likely.

Another evidence of the latter was observed when NaOH was employed for raising pH and negatively charged species such as $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ are predominant. However, the same light blue colour developed with ammonia was observed confirming the ligand exchange mechanism. This observation was first reported by Bois et al. [26] who attributed the blue colour to the “immobilization” of copper onto the surface without further detailed explanations.

Fig. 3 presents the influence of pH on the adsorption of Ag(I) onto APS20% and NN20%. The two solids showed high and similar values of Q_{max} but at different pH ranges.

For NN20% the maximum q values were obtained for pH 3–4 where the predominant specie $[Ag(OH)_2]^-$ interacts with the positively charged amino groups. Lower q values were observed at pH below 3 probably due to the electrostatic repulsion between cationic silver and the protonated silanols and amino groups. At more basic pH (with amino groups neutral and silanol groups negatively charged), higher q values should be expected due to the electrostatic interaction with $[Ag(NH_3)_2]^+$ obtained from ammonia alkalinization. However, the interaction between the amino complexes of Ag(I) and the voluminous N-(2-aminoethyl)-3-aminopropyl groups of the NN series of solids seems to be sterically impeded lowering in this way the retention capacity.

Differently from NN, sorption of Ag(I) onto APS20% reaches a maximum at pH 8–10. In this case the amino groups attached to the silica surface are primary amines instead of the secondary amines of NN and thus, a strong interaction solid/analyte is possible.

From an analytical point of view this distinctive behaviour allows to select, for example, the more suitable solid for Ag(I) sorption when Cu(II) is an interference. In this case, NN at acid pH should be the best choice for silver determination.

Fig. 4 shows the influence of pH on Au(III) sorption onto MPS20%. At pH 2–4, the predominant specie of Au(III) in HCl is $[AuCl_4]^-$ [27,28]. At these values, q is high probably because the electrostatic interaction of the negatively charged gold complex and the protonated silanols, plus a covalent interaction between the gold metallic centre and the thiol groups [29].

At higher pH, q values show a decrease that should be attributed to an electrostatic repulsion between $AuCl_4^-$ and the

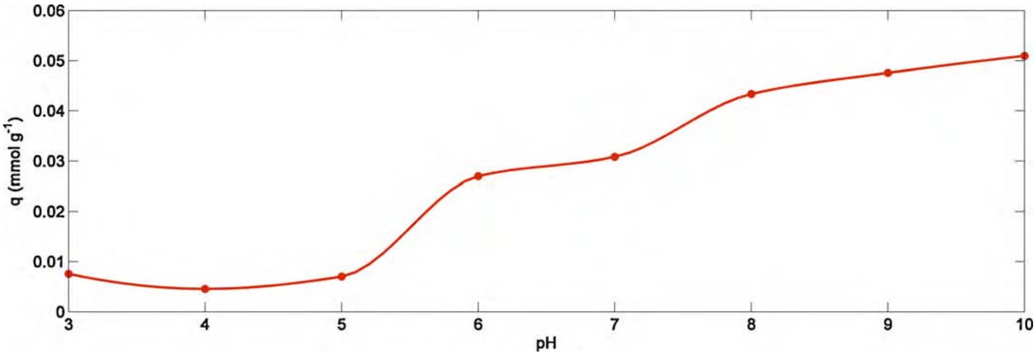

Fig. 2. Influence of pH on Cu(II) adsorption onto APS20%.

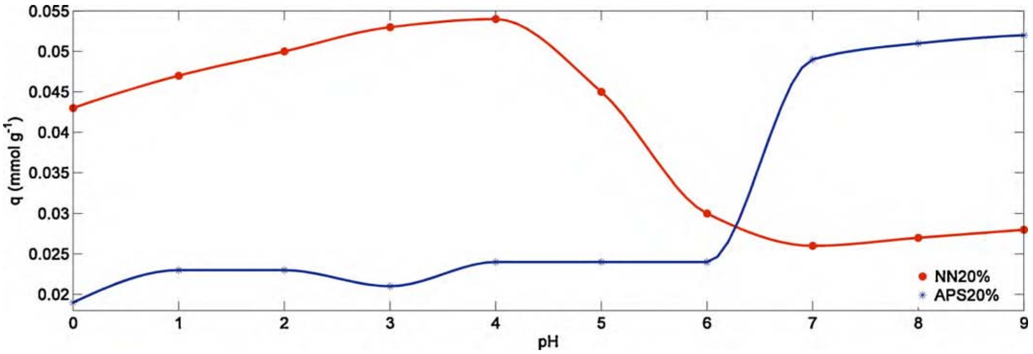

Fig. 3. Influence of pH on Ag(I) adsorption onto APS20% and NN20%.

deprotonated silanols, plus a reduction of the complex into nanoparticles of colloidal gold which are stabilized by the thiol groups on the solid surface [30]. The latter is evidenced by the development of a purple colour (characteristic of colloidal gold) acquired by the solids after 24 h of continuous agitation. So, pH = 2 was chosen for all the experiments throughout this work.

Results from elemental analysis of APS20%, NN20% and MPS20%, showed that each solid presents 1.57, 0.93 and 1.90 mmol g^{-1} of solid of the corresponding functional group. Relating these values with the maximum sorption capacities for Cu/APS, Ag/NN and Au/MPS systems, it was found a ratio (*R*) of 0.25, 0.5 and 0.5 mol of functional group per mol of analyte. These results are in agreement with the coordination numbers found by Lam et al. [31,32] and can be explained by HSAB theory [23–25]. The low value of *R* for Cu/APS should be explained by assuming that the retention of $[Cu(NH_3]^{+2}$ at pH = 9 corresponds to the silanols groups more than to the aminopropyl groups.

Table 2
Kinetic parameters for different analyte/solid systems calculated using PO2.

Analyte/solid system	h (mmol g^{-1} min^{-1})	k_2 (g $mmol^{-1}$ min^{-1})	R^2
Cu(II) + APS20%	0.013	1.59×10^{-5}	0.9989
Au(II) + MPS20%	0.988	2.65×10^{-1}	0.9956
Ag(I) + NN20%	0.003	6.46×10^{-2}	0.9906

3.1.2. Adsorption kinetic studies

Experimental data were modelled through different kinetic models accordingly to Chiron et al. [22]. From all the applied models, Pseudo Second Order model (PO2) showed the best correlation to the experimental data (Table 2).

Results from the adsorption kinetic studies are shown in Figs. 5–7.

When flow systems are employed for analytical purposes, studies on sorption kinetics are mandatory. Particular attention needs to be paid to the initial sorption velocities (*h*, mmol g^{-1} min^{-1}),

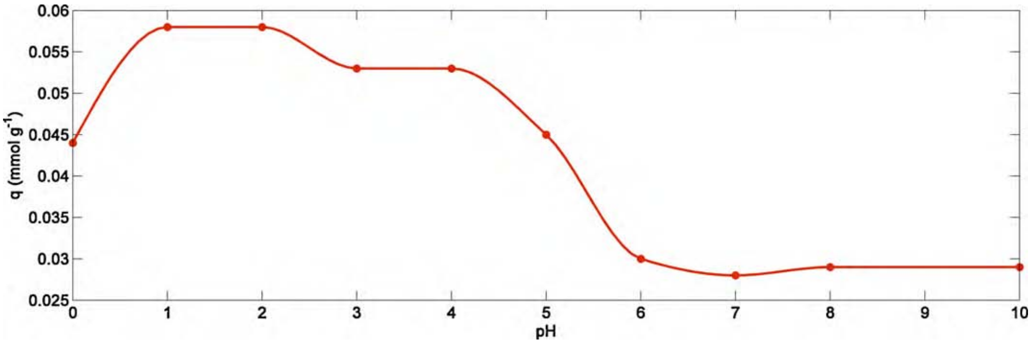

Fig. 4. Influence of pH on Au(III) adsorption onto MPS20%.

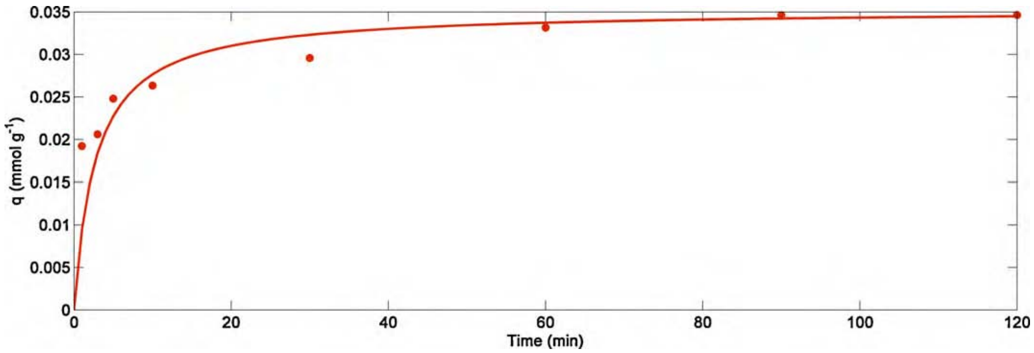

Fig. 5. Adsorption kinetics for Cu(II) ontoAPS20%: comparison of the experimental data with pseudo second order (PO2) kinetic model. Dots: Experimental data, solid line: PO2 calculations.

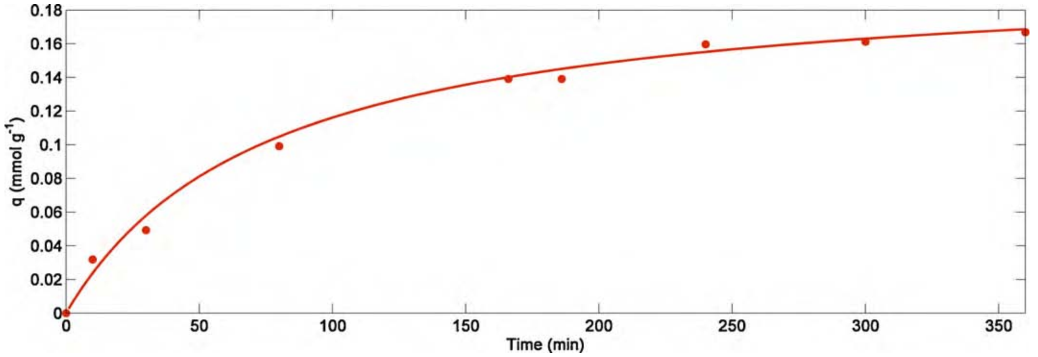

Fig. 6. Adsorption kinetics for Ag(I) onto NN20%: comparison of the experimental data with pseudo second order (PO2) kinetic model. Dots: Experimental data, solid line: PO2 calculations.

Table 3
Optimized elution conditions.

System	Eluent	Eluant volume (μL)	Elution flow rate (mL min^{-1})
Cu + APS	HCl 0.1 mol L^{-1}	80	1.0
Ag + NN	HCl 0.1 mol L^{-1}	1000[a]	1.0
Au + MPS	Thiourea 3% (w/v) in HCl 0.05 mol L^{-1}	400[a]	2.0

[a] Sub-sampling needed for ET AAS.

as they influence the efficiency of solid phase extraction at the short contact times imposed by flow injection (FI) systems [13,19]. Even more, this circumstance becomes particularly important at the moment of reaching specificity since the retention of the analyte can be modulated by changing the time of contact with the solid.

The calculus of *h* values for the three solids with the three analytes gave the following results: for gold *h* MPS20% > APS20% > NN20%; for silver *h* APS20% > NN20% > MPS20%; and for copper *h* APS20% > MPS20% > NN20%.

However Q_{max} and *h* values for the different pairs analyte/solid show some discrepancies at the light of the *HSAB* theory.

In the case of Cu, it was found that $Q_{max\,NN20\%} > Q_{max\,MPS20\%}$ but $h_{MPS20\%} > h_{NN20\%}$. This fact can be explained by steric impediment as copper is retained onto MPS and NN as $[Cu(NH_3)_4]^{2+}$ which is voluminous, making harder its extraction onto a secondary amine

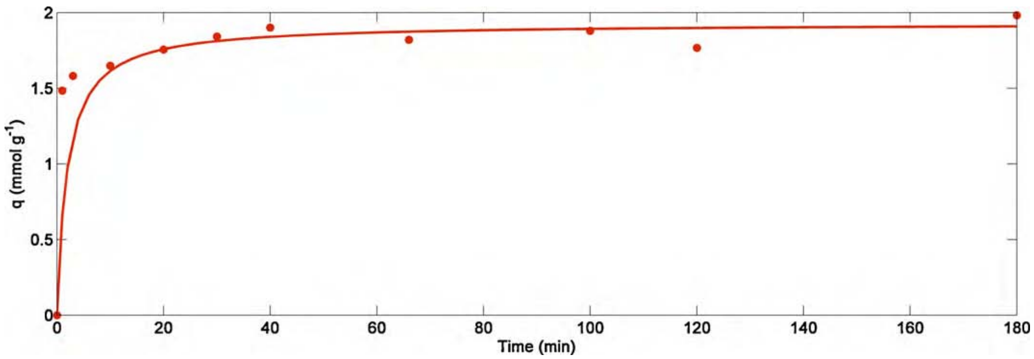

Fig. 7. Adsorption kinetics for Au(III) onto MPS20%: comparison of the experimental data with pseudo second order (PO2) kinetic model. Dots: Experimental data, solid line: PO2 calculations.

at time equal to zero. Ag is retained as $[Ag(NH_3)_2]^+$ but it is smaller than $[Cu(NH_3)_4]^{2+}$ and the steric impediment is, in comparison, less notorious. In consequence $h_{Ag\,NN20\%} \ggg h_{Cu\,NN20\%}$ even though $Q^{Ag}_{max\ NN20\%}$ is lower than $Q^{Cu}_{max\ NN20\%}$.

Once finished the study of the physicochemical properties of the solids in relation to the three analytes the following pairs were selected for analytical purposes using FI-SPE-ET AAS: Cu + APS, Ag + NN and Au + MPS.

3.2. Determination of Cu(II), Ag(I) and Au(III) using FI-SPE-ET AAS

3.2.1. Optimization of elution conditions

For quantitative elution of the analytes, different solutions with acid/base, redox or complexing properties were assayed. Elution volumes were optimized in order to reach the values imposed by ET AAS (about 100 μL) together with high release efficiency. Direct injection of the whole volume of elution into the graphite furnace was performed for the Cu/APS system. However, sub-sampling was needed for Ag and Au as shown in Table 3. In these cases, the eluants were collected in different vessels and then, 80 μL were injected into the furnace.

Even though the elution of Ag(I) with diluted HCl (pH = 1) seems a contradiction as its adsorption onto NN was not despicable (see Fig. 3) at that pH, it is pertinent to recall that the experiment was performed under batch conditions. Flow through scenery (data not shown) revealed a very low adsorption capacity for pH below 2, allowing an easy release of the analyte with HCl at pH = 1. For Au + MPS and Cu + APS systems, no differences in sorption behaviour were observed between batch and FI experiments.

Au + MPS system requires a complexing eluant with acid characteristic for quantitative elution of the analyte. In this case thiourea 3% (w/v) in HCl 0.05 mol L^{-1} was chosen. Thiourea competes with the mercaptopropyl groups of the filling by producing with Au(III) the soluble complex $[AuSHC(NH_2)_2]^{+3}$ whilst HCl changes to positive the charge of the filling, allowing in this way the complete release of gold. Moreover, the selected mixture preserves the life of the solid by keeping a reductive environment and it is ET AAS friendly.

Table 4
Optimized adsorption conditions for all systems.

System	Adsorption flow rate (mL min^{-1})	PCF$_{max}$
Cu + APS	2.0	30
Ag + NN	1.0	10
Au + MPS	2.0	40

3.2.2. Optimization of preconcentration factors (PCF)

PCF is defined as the quotient between the volume of preconcentrated sample and the volume of eluent employed for the analyte liberation in a given extraction system. When FI is employed, PCF reveals the goodness of a particular solid for retaining the analyte under dynamic conditions. In these cases, samples flow rates impose the time of contact analyte/solid and thus the adsorption capacity. On the other hand, the analyte needs to be efficiently released from the solid with a minimal elution volume.

Employing the system in Fig. 1, several sample flow rates were tested in order to obtain a maximum preconcentration factor (PCF$_{max}$). Table 4 shows the optimal adsorption flow rates and PCF$_{max}$ for the three couples analyte/solid. Elution volumes are listed in Table 3.

The values of PCF given in the table for each pair reveal a correlation with the physicochemical data, Q_{max} and h, reported above (see Tables 1a–1c and 2).

Table 5a
Figures of merit for the determination of Au(III) by FI-SPE-ET AAS using MPS20% for MC filling and comparison with other reported methodologies.

Au + MPS20%					
Parameter	Proposed methodology	ET AAS[a]	FI-SPE-FAAS immobilized thiourea in silica gel [33]	FI-SPE-ET AAS with Dowex M4195 [34]	LC-FAAS with polyurethane foams [35]
LOD (μg L^{-1})	0.14	0.88	0.14	1.61	0.01
Sensitivity (μg L^{-1})	0.017	0.0014	509	NR	0.0011
LR (μg L^{-1})	0.45–10	3–80	40–800	NR	0.03–15
FPC	10	–	15–20	31	6.5
RSD % (n = 10, 0.2 μg L^{-1})	3.4	1.3	3.0	<5	2.9
MC lifetime (cycles)	>200	–	1000	100	NR
Sample throughput (h^{-1})	8	30	24	15	0.33

NR: Not reported.

[a] Measured in our laboratory.

Table 5b
Figures of merit for the determination of Cu(II) by FI-SPE-ET AAS using APS20% for MC filling and comparison with other reported methodologies.

Cu + APS20%					
Parameter	Proposed methodology	ET AAS[a]	FI-SPE-TS-FF-AAS with XAD4-DHB [36]	FI-SPE-ET AAS with silk fibroin [37]	FI-SPE-FAAS using biosorbents [38]
LOD (μg L^{-1})	0.02	0.18	0.1	0.008	3
Sensitivity (μg L^{-1})	0.06	0.60	0.0910	0.3389	0.0035
LR (μg L^{-1})	0.06–5	0.6–20	1–5	0.025–1.5	16–100
FPC	10	–	62	27.3	16
RSD % (n = 10, 0.2 μg L^{-1})	2.7	1.5	3.1	2.2	3.3
MC lifetime (cycles)	>100	–	NR	NR	100
Sample throughput (h^{-1})	8	30	40	18	12

NR: Not reported.

[a] Measured in our laboratory.

Table 5c
Figures of merit for the determination of Ag(I) by FI-SPE-ET AAS using NN20% for MC filling and comparison with other reported methodologies.

Ag + NN20%					
Parameter	Proposed methodology	ET AAS[a]	FI-D/SPE-FAAS [39]	FI-SPE-ICP-AES with CCTS-DHBA [40]	SPE-FAAS in cellulose nitrate disks [41]
LOD ($\mu g\,L^{-1}$)	0.025	0.26	0.2	0.08	4.6
Sensitivity ($\mu g\,L^{-1}$)	0.329	0.033	0.0111	543.1	NR
LR ($\mu g\,L^{-1}$)	0.075–10	0.9–30	0.5–30	0–5	250–5000
FPC	10	–	110	8.3	5–10
RSD % ($n = 10$, 0.2 $\mu g\,L^{-11}$)	3.0	1.3	3.1	0.5–4	3.0
MC lifetime (cycles)	>200	–	Unlimited	NR	–
Sample throughput (h^{-1})	6	30	19	7	3

NR: Not reported.

[a] Measured in our laboratory.

Table 6
MTL interferences on the determination of Au(III), Cu(II) and Ag(I) under optimized conditions. FPC = 10, [Au(III)] = 10 $\mu g\,L^{-1}$, [Cu(II)] = 4.5 $\mu g\,L^{-1}$, [Ag(I)] = 0.5 $\mu g\,L^{-1}$, $n = 5$.

	Au + MPS20%		Cu + APS20%		Ag + NN20%	
Interference	MTL ($\mu g\,L^{-1}$)	Recovery (%)	MTL ($\mu g\,L^{-1}$)	Recovery (%)	MTL ($\mu g\,L^{-1}$)	Recovery (%)
Au(III)			10	102 ± 2	100	99 ± 2
Cu(II)	100	95 ± 1			100	101 ± 1
Ag(I)	100	98 ± 3	50	100 ± 1		
Al III)	1000	99 ± 2	100	97 ± 2	100	97 ± 2
Zn(II)	1000	99 ± 2	100	101 ± 2	100	99 ± 2
Fe(III)	500	98 ± 1	10	100 ± 1	1000	100 ± 1
Mg(II)	100,000	98 ± 1	100,000	100 ± 1	10,000	99 ± 1
Ca(II)	10,000	97 ± 1	10,000	101 ± 2	50,000	97 ± 2
Na(I)	50,000	96 ± 1	10,000	99 ± 1	10,000	98 ± 1
K(I)	10,000	97 ± 1	10,000	101 ± 1	10,000	99 ± 1
$PO_4{}^{3-}$	50,000	96 ± 2	50,000	100 ± 1	100,000	100 ± 1
Cl^-	10,000	98 ± 2	10,000	98 ± 2	50,000	100 ± 2
$SO_4{}^{2-}$	10,000	99 ± 1	50,000	101 ± 2	50,000	100 ± 1

3.2.3. Comparison of the analytical performance

The three systems were compared between each other and with other methodologies already reported. The PCF was kept equal to 10 and then, the main analytical figures of merit were obtained. Limits of detection (LOD), sensitivity, linear range (LR), MC lifetime and relative standard deviation (RSD %) were calculated for $n = 10$ and analyte concentration in the sample equal to 0.2 $\mu g\,L^{-1}$.

Particularly for gold, an excellent performance was obtained in comparison to other methodologies already reported (Tables 5a–5c). Copper and silver determinations showed figures of merit better or similar to those reported in the literature. Nonetheless, the analytical methodology described here seems simpler.

3.2.4. Study of anionic and cationic interferences on analytes adsorption onto APS, NN and MPS solids

A study of cationic and anionic interferences of usual occurrence in natural waters was carried out. The effects of concomitant anions and cations in binary solutions were assessed. Results are summarized in Table 6, where maximum tolerable limits (MTL) mean the maximum concentration of the interference that allows the quantitative recovery of the analyte.

As seen in Table 6 for Au(III), neither Ag(I) nor Cu(II) revealed themselves as serious interferences on the determination of Au(III) at pH 2. Since Cu(II) and Ag(I) showed negligible sorption capacities (0.0075 and 0.02 $mmol\,g^{-1}$, respectively) together with low h values, specific gold determination was easily performed under dynamic conditions.

Since silanols from MPS provide a negative surface charge, the tolerance to anions is relatively high. The elevated values of MTL found for cations should be attributed to the absence of attractive interactions with mercaptopropyl groups and/or to low times of contact concomitant/filling under flow through conditions.

Regarding Cu(II) and Ag(I), both analytes showed an efficient adsorption onto APS at high pH values and long contact times (see Figs. 2 and 3). Moreover calculated $h_{\mathrm{Ag(I)}}$ was higher than $h_{\mathrm{Cu(II)}}$ (2.505 and 0.013 $mmol\,g^{-1}\,min^{-1}$, respectively). In this way, Ag(I) becomes a serious interference for Cu(II) determination regardless it is performed under batch or flow through operation. The interference of Au(III) is not relevant due to the precipitation of Au(III) at pH 9.

Amphoteric cations show no influence on Cu(II) and Ag(I) determination probably because they exist as anions at the selected pH and thus, they are electrostatically repelled by the solid.

The adsorption of Ag(I) onto NN20% showed high specificity at the optimal conditions since its adsorption is highly favored by adsorption kinetics.

4. Concluding remarks

In this work, the sorption and kinetic behaviours of ions from group IB onto different hybrid mesoporous solids were studied.

The importance of understanding the type of interaction analyte/filling under non-thermodynamical equilibrium conditions (dynamic regime of sorption, kinetically controlled) provided for FI systems, was exemplified through the development of three different analytical methodologies for the determination of traces of gold, copper and silver.

In this way, we have shown that it is possible to design sorbent materials able to perform the specific determination of a given specie by simply combining the characteristics of the solid material with the dynamic conditions imposed by the flow systems (kinetic discrimination) and a detector working under continuous (preferably) or discrete operation.

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