



Flow injection solid phase extraction electrothermal atomic absorption spectrometry for the determination of Cr(VI) by selective separation and preconcentration on a lab-made hybrid mesoporous solid microcolumn[☆]

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ABSTRACT

A lab-made hybrid mesoporous solid was employed in a flow injection solid phase extraction electrothermal atomic absorption spectrometric (FI-SPE-ETAAS) system for the selective retention of Cr(VI). The solid was prepared by co-condensation of sodium tetraethylortosilicate and 3-aminopropyltriethoxysilane by sol-gel methodology and one-pot synthesis and characterized by Fourier transform infrared spectroscopy, X ray diffraction spectroscopy, and scanning electronic microscopy. Adsorption capacities at different pH values of both, Cr(VI) and Cr(III), were also measured in order to obtain the optimum retention for Cr(VI) with no interference of Cr(III). The maximum capacity of adsorption (4.35 mmol g^{-1}) was observed for pH values between 2–3, whilst Cr(III) was found to remain in solution (adsorption capacity = $0.007 \text{ mmol g}^{-1}$). Then, a microcolumn (bed volume: $7.9 \mu\text{L}$) was filled with the solid and inserted in the FI-ETAAS system for analytical purposes. Since the analyte was strongly retained by the filling in the anionic form, 0.1 mol L^{-1} hydroxylammonium chloride in 1 mol L^{-1} hydrochloric acid was selected as eluent due to its redox characteristics. In this way, the sorbed Cr(VI) was easily released in the cationic form. The enrichment factor (EF) was found as a compromise between sensitivity and sample throughput and a value of 27 was obtained under optimized conditions: pH 2, sample loading 2 mL min^{-1} (60 s), elution flow rate 0.5 mL min^{-1} (eluent volume: $75 \mu\text{L}$).

Under optimized conditions the limit of detection for Cr(VI) was 1.2 ng L^{-1} , the precision, expressed as RSD was 2.5%, the sample throughput 21/h, and the microcolumn lifetime was over 300 adsorption/desorption cycles.

Cr(III) determination was also performed by simply measuring its concentration at the end of the column and after Cr(VI) retention by the mesoporous solid.

Applications of the methodology to the determination of Cr(VI) in deionized, osmosis, mineral, effluent and river waters showed very good results. Validation was performed by means of recovery studies as no certified materials were available for Cr(VI). Total chromium determinations, obtained by the sum of Cr(III) and Cr(VI) concentrations, were validated using NIST, SRM 1643e certificate reference material (Trace Element in Natural Water).

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1. Introduction

Research purposes, industrial applications and ecotoxicological concerns are some of the fields where the determination of chromium at trace levels has found considerable interest. Chromium is mainly found in solution in two oxidation states, III and VI, both showing well differentiated chemical properties and environmental consequences.

While Cr(III) is normally an acidic cation with non-remarkable redox behaviour and an essential element for many biological mechanisms, Cr(VI) is always found as an anion and presents a high toxicity for the biota. Therefore, it is of increasing importance to accurately define the individual quantity of both species.

Flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma-mass spectrometry (ICP-MS) can only yield total amount of chromium. As a result, preliminary species separation and pre-concentration are required before the determination by any of the above mentioned techniques.

Flow injection analysis (FIA) appeared as a powerful tool for on-line operations, such as separation and pre-concentration. The coupling to

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high performance detectors, such as ETAAS, extends these capacities to the field of ultratrace analysis. Several FI–ETAAS systems involving different strategies for separation and pre-concentration have been described in the literature [1,2]. Among these strategies, the solid phase extraction (SPE) in packed microcolumns is one of the most popular ones [3–5]. In the last few years, the analytical applications of the hybrid mesoporous materials have been increased due to their remarkable characteristics such as large surface area, easiness of functionalization, high adsorption capacity and chemical and mechanical resistance [6]. Mesoporous solids have been used extensively for isolation of metals from complex matrix samples in remediation systems [7,8]. However, only very few works have shown an efficient use of these materials for on-line solid phase extraction followed by elemental determination at ultratrace levels [9–11], probably due to the necessity to include multiple and time consuming steps to perform the retention, elution and detection of the analytes of interest.

The main objective of this work is to present the employment of the mesoporous silica MCM-41 functionalized with 3-aminopropyl groups (APS) for analytical applications. In this way, a FI–SPE–ETAAS system holding a microcolumn (MC) filled with the functionalized silica was employed to perform automatically the operations described above. The hybrid mesoporous solid was synthesized in our laboratories by the One Pot procedure employing Sol–Gel methodology and then, characterized through Fourier Transform infrared (FTIR) and X Ray Diffraction (XRD) spectroscopy and scanning electron microscopy (SEM). The influences of the percentages of functionalization and the acidity of the medium on the adsorption capacity of the analyte, together with kinetic studies at the optimal pH of adsorption were also investigated.

Cr(VI) was retained in the column in anionic form and eluted with hydroxylammonium chloride in hydrochloric acid solution. In this way, the adsorbed Cr(VI) was easily released in the cationic form with no significant retention of Cr(III) by the solid. Consequently, and taking advantage of the higher concentration of Cr(III) in natural waters, it was measured directly at the end of the column after the retention of Cr(VI).

Optimal conditions of operation will be discussed together with the influence of cationic and anionic interferences on the analytical signal. Applications to the determination of Cr(VI) and Cr(III) in different kind of natural waters will be shown. The accuracy of the proposed method will be demonstrated by recovery experiments and the determination of total chromium in SRM 1643e Trace Elements in Natural Waters as certified reference material.

2. Experimental

2.1. Reagents and materials

All the reagents listed below were of analytical grade. Doubly deionized water (DIW, 18 M Ω cm) obtained from a Milli-Q water System (Millipore, Bedford, MA, USA) was used throughout. Sodium tetraethylortosilicate (TEOS) 98% ($M=208.33$, $d=0.934$ g mL $^{-1}$), cetyl-trimethylammonium bromide (CTAB) ($M=364.46$) and 3-aminopropyltriethoxysilane (APTES) ($M=221.37$, $d=0.942$) were obtained from Sigma Aldrich (St Louis, MO, USA). HCl 38% (w/w) and NaOH (s) were obtained from Merck (Darmstadt, Germany). All standard solutions were prepared by adequate dilution of stock standard solutions of 1.000 mg L $^{-1}$ (Merck). All operations were performed on a laminar flow clean bench. Nalgene (Nalge, Rochester, NY, USA) laboratory ware was thoroughly cleaned with (1 + 1) nitric acid and rinsed with DIW. Before pre-concentration, Cr(VI) and Cr(III) standard solutions and water samples were kept at pH 2 by the addition of a suitable amount of HCl and made up to volume with DIW. For preparing the eluent, 0.7 g of hydroxylammonium chloride (HC) (Merck) were dissolved in 100 mL of 1 mol L $^{-1}$ HCl.

2.2. Apparatus

XRD patterns were collected in h–2h mode using a conventional goniometer (Siemens D5000) with a Cu K α_1 radiation source. FTIR spectra were collected using a Nicolet Magna 560 spectrometer using KBr pellets for sample preparation. SEM micrographs were taken using a Zeiss DSM 982 Gemini (Carl Zeiss, Jena, Germany). For chromium determinations, a Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory GFA 6000 and an autosampler ASC-6000 was used. A Hamamatsu hollow cathode lamp was employed as radiation source at 214.3 nm with a slit width of 2 nm and 10 mA lamp current. The measurements were performed in integrated absorbance (peak area). Standard pyrolytically coated graphite tubes (Shimadzu) were used. The furnace temperature program for chromium determination is given in Table 1. High purity argon was used as the internal gas (AGA, Argentina).

2.3. Preparation of functionalized mesoporous silica (APS)

The solid APS was prepared according to the methodology described in a previous work [9]. The molar composition of the solids was kept in a relation of 0.12 CTAB:0.5 NaOH:1 – x TEOS: x APTES: 130 H $_2$ O (with x ranging between 0–0.2). The surfactant (CTAB) was dissolved in NaOH and DIW. In a separate vessel, APTES and TEOS were mixed in different molar proportions (0–20%, expressed in percentages) (ranging from 0 to 20% m/m) and then, they were added to the first solution slowly and under continuous agitation. Afterwards, the mixture was agitated for 24 h at 25 °C and the solid was filtrated, washed and dried in a vacuum desiccator. The surfactant extraction was performed refluxing the solid with HCl in ethanol. Finally, it was washed again with ethanol and DIW and dried in the vacuum desiccator.

2.4. Study of the influence of pH on the adsorption of Cr(VI) and Cr(III) on APS

To study the influence of pH on Cr(VI) adsorption at percentages of functionalization ranging between 5 and 20%, 5 mL of a solution containing 5 mg L $^{-1}$ Cr(VI) at different pH values were suspended in 0.05 g of APS (the experiment was repeated for the different proportions APTES/TEOS), agitated for 24 h at 25 °C and centrifuged at 3000 rpm. 2 mL of the supernatant were taken and the remaining amount of Cr(VI), and thus the quantity adsorbed by the solid, was determined by FAAS. The different pH values, ranging between 0–9 were obtained by the addition of 1 mol L $^{-1}$ HCl or 1 mol L $^{-1}$ NaOH. The same experiment was repeated for solutions containing 5 mg L $^{-1}$ Cr(III).

2.5. Kinetic studies on the adsorption of Cr(VI) onto APS

A portion of 0.1 g of the sorbent was equilibrated with 500 mL of 15 μ g L $^{-1}$ Cr(VI) at pH = 2. Aliquots of 100 μ L of the supernatant were collected at different times with a 1000 μ L Springer Hamilton syringe, filtered through a 0.45 μ m membrane and determined by ETAAS.

Table 1
Graphite furnace temperature program for the determination of chromium.

Step	Temperature (°C)	Ramp time(s)	Hold time (s)	Ar flow (mL min $^{-1}$)
Drying	100	30	–	0
Drying	120	30	–	0.5
Drying	120	–	5	1
Pyrolysis	500	39	–	1
Pyrolysis	500	–	5	0
Atomization	2400	–	3	0
Cleaning	2600	–	2	0.2

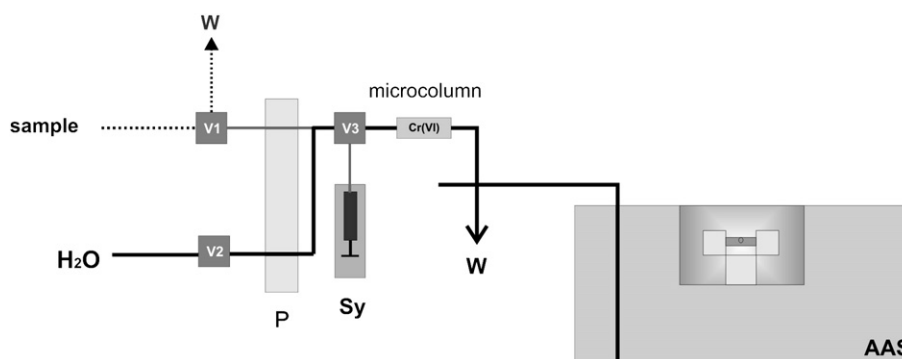


Fig. 1. Flow injection manifold in sample loading position (see text for sequence of operations). P, peristaltic pump; V1, valve 1; V2, valve 2; V3, valve 3; Sy, autosampler syringe; W, waste; ETAAS, Electrothermal atomic absorption spectrometer; Microcolumn packed with APS for Cr(VI) retention.

(Note that the taken volumes are neglectable in comparison to the whole volume of supernatant solution).

Adsorption efficiency (q) was expressed as the quantity of adsorbed Cr(VI) per unit of adsorbent mass. It was calculated as: q (mmol g^{-1}) = $(C_0 - C)/m$, where C_0 and C are the initial and residual concentration of Cr(VI), respectively, and m is the mass of sorbent.

For studies on adsorption kinetics of these kinds of solids, four different models were analyzed as suggested in the literature [12]. Pseudo-first order, pseudo-second order, double exponential and Langmuir models were applied by using the mathematical equations described in the work mentioned above.

2.6. Analytical procedure for Cr(VI) and Cr(III) determinations

The pre-concentration system is shown in Fig. 1. The microcolumn was constructed from an acrylic cylinder (3.0 cm long, 1.6 cm diameter) furnished with 0.25–28 female connectors. The inner part was drilled to obtain a 7.9 μL bed volume (10 mm long, 1.0 mm id). The aspect ratio (length to diameter) was adjusted to keep minimal dispersion in the system together with lower resistance to the flow stream. The microcolumn was slurry loaded with the solid by means of a syringe and used for over 300 enrichment cycles before repacking. Two plugs of polystyrene foam were placed at both sides of the filling in order to retain the solid. The FI manifold was assembled with zero dead volume Cheminert fittings (Valco Instruments, Houston, TX) and PTFE tubing (0.5 mm id). An Ismatec MS Reglo (Ismatec, Glattbrugg, Germany) four channels, six rollers peristaltic pump was used. The pump was controlled via the analogue external port. Tygon tubes were used for pumping all the solutions. Three-way solenoid valves (Cole Parmer, IL) were employed to switch streams. V1 and V2 were PEEK zero dead volume solenoid valves (one inlet, two outlets); V3 was a PTFE manifold valve with two inlets and one outlet. An eight independent relays circuit controlled through the serial port of the computer switched the valves and pump. Interfacing of the FI system to the graphite furnace was achieved by simply connecting one inlet of V3 to the autosampler syringe and the V3 outlet to the sample introduction capillary of the autosampler arm [13]. Cr(III) determinations were performed by collecting the solution eluted at the end of the microcolumn (see Fig. 1) and injecting it directly, once the automatic cycle was finished.

3. Results and discussion

3.1. Characterization of sorbents

3.1.1. IR spectra of sorbents

IR spectra of the solids APS 15%, APS 20% and silica MCM-41 showed peaks around 1100 cm^{-1} and 3200–3400 cm^{-1} attributed to Si–O–Si and O–H stretching vibrations respectively, and bands around 800 cm^{-1} attributed to Si–O vibrations. The spectra indicated the

occurrence of silica matrices in the three materials. The absorption peaks revealed at 1630 cm^{-1} belong to the ν_{OH} vibration of adsorbed water. On the other hand, the IR spectra of APS 15% and 20% when compared to the IR spectrum of silica MCM-41 (blank), revealed peaks around 2800–3000 cm^{-1} corresponding to the typical C–H stretching vibrations of aliphatic chains of aminopropyl groups.

3.1.2. XRD spectra of sorbents

XRD spectra of sorbents showed a broad band centered in $2\theta = 2$ in agreement with the disposition of mesoscopic pores in hexagonal structures. It was observed that the peak broadens with increasing percentage of functionalization. From 20% of functionalization onwards, the solids were amorphous and were not considered for adsorption studies. On the other hand, the diffraction patterns of APS 5% showed no significant differences in comparison with the blank and were not considered. In all cases, D_{100} values (Table 2) were in agreement with those reported by Yokoi et al. [14].

3.1.3. SEM of sorbents

Fig. 2a and b show the SEM micrographs of the solids APS 20% and APS 40%. As told in the previous section, the solids with percentages of functionalization above 20% showed amorphous characteristics. However, the solids functionalized with aminopropyl amounts between 5% and 20% revealed disc-like shapes with diameters close to 0.80 μm .

3.2. Influence of pH on the adsorption of Cr(VI) on APS

Once the mesoporous solids with different percentages of functionalization were obtained, it was necessary to optimize their surface charge by changing the pH of the solutions in contact with them. Fig. 3 shows the influence of pH on the retention of Cr(VI) and Cr(III) at the microcolumn packed with APS 20%. Results for solids containing lower proportions APTES/TEOS are not shown as poorer sorption capacities were observed for Cr(III) and Cr(VI) at any pH value. The maximum capacity of adsorption for Cr(VI) onto APS 20% was observed for pH values between 2 and 3, which is in agreement with those reported by Lam et al. [15]. In this range, Cr(VI) adsorption capacity was 4.35 mmol g^{-1} and that of Cr(III) was 0.007 mmol g^{-1} . These values reveal that APS 20% at pH 2 is highly selective for Cr(VI) retention (actually in the form HCrO_4^- at the chosen pH) allowing its

Table 2
 D_{100} values for the different solids using Bragg's Law.

Sample	2θ ($^\circ$) maximum	D_{100} (nm)
MCM-41	2.108	4.187
APS 10%	1.969	4.484
APS 15%	1.940	4.549
APS 20%	1.878	4.699

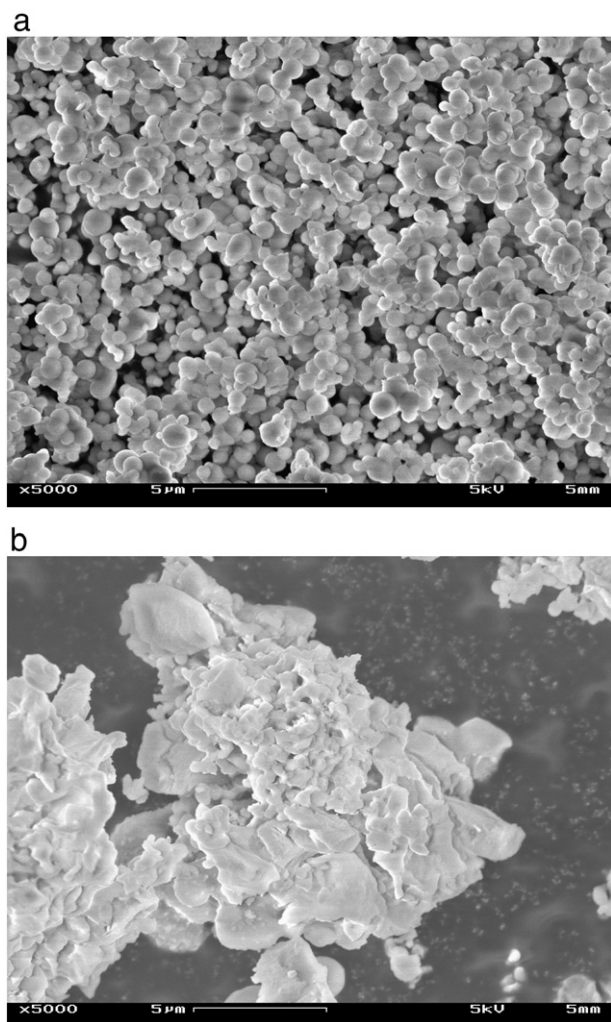


Fig. 2. a) SEM image of APS 20%, b) SEM image of amorphous silica functionalized with 40%.

pre-concentration with no interference of the cationic form and thus, making possible the sequential determination of both species.

3.3. Kinetic studies on the adsorption of Cr(VI) on APS

Fig. 4 shows the dependence of the adsorption capacity q (obtained as described under 2.6) on the contact time between the adsorbent and the analyte solution. As can be seen, the Langmuir model (dashed line) fits quite well the experimental data (dotted line) and becomes the model that best describes the kinetics of adsorption for long contact times. From these data, the kinetic parameter $K_L = 2.39 \text{ L mmol}^{-1}$

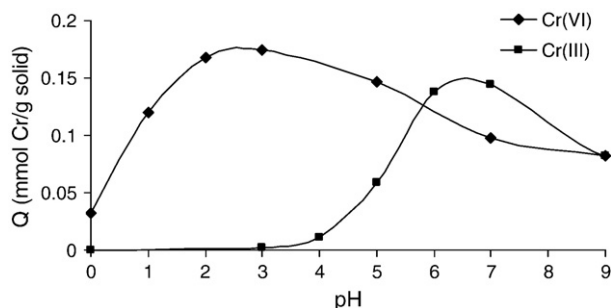


Fig. 3. Influence of pH on the adsorption of Cr(VI) and Cr(III) onto APS 20%. [Cr(VI)] and [Cr(III)]: 5 mg L^{-1} , 5 mL of solution in 0.05 g of APS.

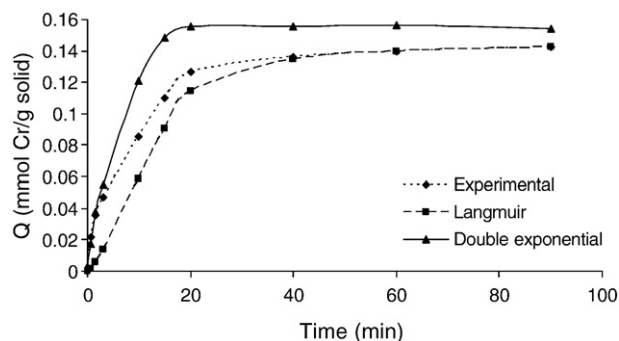


Fig. 4. Adsorption kinetics for Cr(VI) (onto APS 20%) at pH=2. Experimental data compared to Langmuir and double exponential models.

with $K_d N$ value of 10^{-6} min^{-1} was obtained (K_d is the desorption rate and N the maximum number of adsorption sites occupied by the metal). These values together with the extremely low adsorption capacity of the solid for Cr(III), allow us to conclude that the active sites of the adsorbent have a great affinity for the analyte (HCrO_4^- ions).

Maybe for short contact times, the double exponential model (full line) allows a better description of the experimental results based on the occurrence of two different mechanisms for sorption. The first mechanism supposes an electrostatic interaction between the anion and the protonated aminopropyl groups on the surface [9]. The second assumes a diffusion-controlled mechanism between the active sites on the surface and those inside the mesopores. As FI systems are based on kinetic phenomena at short times, the double exponential model makes a better description of the sorption process.

3.4. Optimization of the separation and pre-concentration step

In order to optimize the pre-concentration step and to adequate the elution volumes to the graphite furnace needs, the microcolumn was designed to keep dispersion at a minimum. The volumetric flow rate for sorption of Cr(VI) onto the filling was varied between 0.5 and 4 mL min^{-1} . Higher values were not employed as leaks were observed as a consequence of compaction of the mesoporous solid and the development of internal pressures in the system. Lower values were not compatible with the proper operation of the peristaltic pump. Experiments were performed with a $0.5 \mu\text{g L}^{-1}$ Cr (VI) solution at pH=2 with a constant pre-concentration factor (PCF) equal to 27.

A volumetric flow rate of 2 mL min^{-1} was chosen as the most advantageous (see Fig. 5). Lower values produce a low sample throughput. Higher values decrease the time of contact between the filling and the analyte and thus the chance of retention. Regarding the desorption flow rate, any value below 2 mL min^{-1} allowed full recovery of the analyte (Fig. 5); however, a desorption flow rate of 0.5 mL min^{-1} was selected as a compromise between the maximum

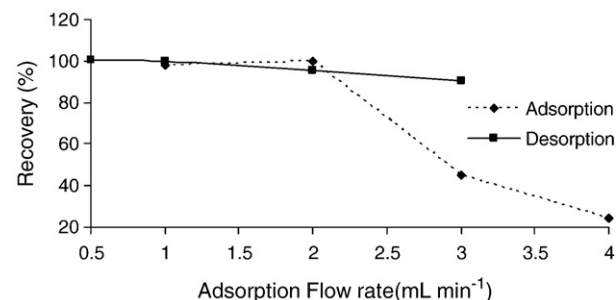


Fig. 5. Optimization of adsorption and desorption flow rates of Cr (VI) solutions. [eluent]: 0.1 mol L^{-1} HC in 1.0 mol L^{-1} HCl, [Cr(VI)]: 500 ng L^{-1} , FPC=27.

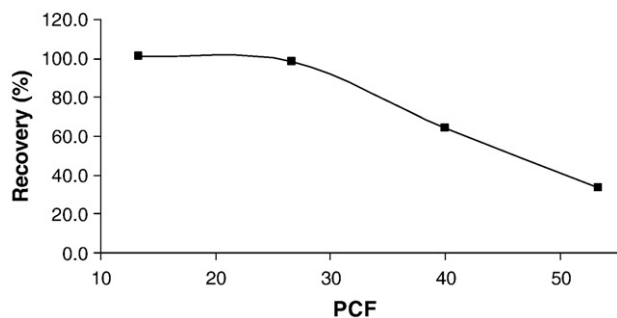


Fig. 6. Determination of maximum PCF. [eluent]: 0.1 mol L⁻¹ HC in HCl 1.0 mol L⁻¹, [Cr(VI)]: 500 ng L⁻¹, adsorption flow rate: 1 mL min⁻¹, desorption flow rate: 0.5 mL min⁻¹.

volume compatible with the graphite furnace operation and the contact time between analyte and eluent.

Fig. 6 shows the percentage of recovery of 0.5 µg L⁻¹ Cr(VI) for different PCF values. As can be seen, at PCF values around 27, a 100% recovery of Cr(VI) was found. From PCF 27 onwards an important decay was observed revealing that all sites of sorption were already covered by the analyte. Column properties remained the same for over 300 cycles of pre-concentration.

3.5. Elution

Regarding the complete release of adsorbed Cr(VI), a mixture of 0.1 mol L⁻¹ hydroxylammonium chloride in 1 mol L⁻¹ hydrochloric acid was found as a very suitable eluent. This mixture allowed fast reduction of Cr(VI) to Cr(III) together with the complete release of the analyte in a volume of 75 µL, which is fully compatible with the graphite furnace operation. Moreover, the oxidation products of the eluent are highly volatile and can be easily removed during the dry and pyrolysis stages with no interference during atomization. Chromium is retained in the anionic form and released as a cation since the filling remains protonated all along the measurements. Additionally, as Cr(III) is not retained on the APS filling while Cr(VI) is completely extracted, the former was directly determined by measuring its concentration at the end of the column after Cr(VI) pre-concentration.

Table 3

Analytical features and figures of merit of the proposed methodology: comparison with other values already reported.

Parameter	Present work		SI-BI-LOV [16]	FI-SPE on PCTFE-beads [17]	SIA-SPE on <i>Chlorella vulgaris</i> cells [18]	
	Cr(VI)	Cr(III)	Cr(VI)	Cr(VI)	Cr(VI)	Cr(III)
Detection system	ET AAS		ET AAS	FAAS	ET AAS	
Regression equation (µg Cr L ⁻¹)	1.551[Cr] + 0.001	0.062[Cr] + 0.002	N.R.	N.R.	N.R.	N.R.
Sensitivity (µg ⁻¹ L)	1.551	0.062	0.27	0.0047	0.003	0.17
LOD (µg L ⁻¹) ^a	0.0012	0.03	0.03	0.4	0.03	0.02
RSD %, n = 10	2.5 ^a	1.5 ^b	3.8	1.8	2.5	1.9
Linear range (µg L ⁻¹)	0.004–0.5	0.10–10	0.01–1.25	1–50	0.12–2.0	0.1–2.5
Sample throughput (h ⁻¹)	21		15	30	N.R.	N.R.
Column lifetime (cycles)	>300		Renewable	N.R.	N.R.	N.R.
Preconcentration time (s)	60	–	12.9	90	N.R.	N.R.
Enhancement factor	27	–	30.1	94	11.6	10.5

N.R. Not reported.

^a RSD % calculated at 0.50 µg L⁻¹ Cr(VI).

^b RSD % calculated at 5 µg L⁻¹ Cr(III).

Table 4

Studies of Cr(VI) recovery in presence of cationic and anionic interferents (0.25 µg L⁻¹ Cr(VI)).

Interferent	Concentration (µg L ⁻¹)	Recovery (%)
Cr(III)	20	96
	50	108
Fe(III)	100	112
	500	120
Al(III)	100	92
	500	90
Cu(II)	100	108
	500	90
Zn(II)	100	100
	500	100
Ca(II)	50000	100
	100000	100
Mg(II)	10000	100
	50000	96
Na(I)	20000	116
	40000	116
Sulfate	100000	116
	1000000	112
Nitrate	100000	90
	1000000	96
Chloride	30000	116
	60000	116
Phosphate	100000	116
	1000000	120

The features of the FI system and the figures of merit of the determination are listed in Table 3 and compared with reported values [16–18].

3.6. Study of anionic and cationic interferences on Cr(VI) sorption

A study of cationic and anionic interferences of usual occurrence in natural waters was carried out employing the analytical method described in this paper. Cr(III), Al(III), Fe(III), Zn(II), Cu(II), Ca(II), Mg(II), Na(I), chloride, nitrate, sulfate and phosphate solutions with concentrations up to 10 times higher than those of river water were investigated. Recoveries of Cr(VI) are listed in Table 4.

3.7. Applications

Recovery experiments were carried out in order to investigate the goodness of the proposed methodology. Deionized, osmosis, mineral, effluent and river water were spiked with 0.25 µg L⁻¹ Cr(VI) solutions and then analyzed. Recoveries of Cr(VI) are shown in Table 5.

Results showed an excellent recovery of Cr(VI) in DIW, osmosis and mineral water samples. In these cases, Cr(VI) determinations can be performed by simple interpolation of the analytical signal in the calibration graph (Table 5). Cr(III) was also determined at the end of the microcolumn by simple interpolation of the signals into the

Table 5

Analytical results for water samples spiked with Cr(VI).

Sample	Cr(VI) added (0.25 µg L ⁻¹)	Cr(III) found (µg L ⁻¹)	Cr(VI) found (µg L ⁻¹)	Recovery Cr(VI) %
DIW	0	N.D.	N.D.	–
	0.25	N.D.	0.25 ± 0.05	100
Osmosis	0	0.33 ± 0.01	0.03 ± 0.01	–
	0.25	0.33 ± 0.01	0.29 ± 0.01	104
Mineral	0	0.34 ± 0.01	0.02 ± 0.01	–
	0.25	0.37 ± 0.01	0.28 ± 0.01	104
Effluent	0	0.59 ± 0.01	0.05 ± 0.02	–
	0.25	0.75 ± 0.05	0.26 ± 0.05	84
River	0	0.76 ± 0.05	0.05 ± 0.01	–
	0.25	0.81 ± 0.05	0.24 ± 0.01	76

N.D. Not detectable.

Number of replicates: 5.

working curve (Table 5). For effluent and river water samples, Cr(VI) recoveries were lower than 100% and the standard addition technique needs to be applied.

As it was not possible to employ certified reference material for Cr(VI) and Cr(III) species in water, both species were determined in NIST 1643e (Trace Elements in Water, certified value: $20.40 \pm 0.24 \mu\text{g L}^{-1}$ of Cr) following the proposed methodology. The sum of both results was in good agreement with the certified values ($20.38 \pm 0.10 \mu\text{g L}^{-1}$ total chromium).

4. Conclusion

In this work, we present for the first time a fully automatic FI-SPE-ETAAS system for Cr(VI) and Cr(III) determination employing a lab-made organic-inorganic mesoporous solid with aminopropyl groups functionalization and with pre-concentration properties. After characterization, APS 20% was selected as it showed the highest capacity for Cr(VI) retention with no interference from Cr(III). This selectivity, easily explained by the cationic surface charge of APS at pH 2, was extended to other anions present in real samples. In this case, the selectivity was explained considering the fast adsorption kinetics of the analyte in comparison to other negatively charged interferents. The analytical methodology was successfully applied to the speciation analysis of inorganic chromium in different kind of water samples, revealing the high versatility of these solids when used together with systems allowing reproducible and precise timing of manipulation.

Acknowledgments

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