



Non-chromatographic determination of ultratraces of V(V) and V(IV) based on a double column solid phase extraction flow injection system coupled to electrothermal atomic absorption spectrometry

Manuela Leticia Kim, Mabel Beatríz Tudino*

Laboratorio de Análisis de Trazas, Departamento de Química Inorgánica, Analítica y Química Física, INQUIMAE, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, (1428) Buenos Aires, Argentina

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ABSTRACT

In this work, a non-chromatographic procedure for the on-line determination of ultratraces of V(V) and V(IV) is presented. The method involves a solid phase extraction-flow injection system coupled to electrothermal atomic absorption spectrometry (SPE-FI-ETAAS). The system holds two microcolumns (MC) set in parallel and filled with lab-made mesoporous silica functionalized with 3-aminopropyltriethoxy silane (APS) and mesoporous silica MCM-41, respectively. The pre-concentration of V(V) is performed by sorption onto the first MC (C1) filled with APS at pH 3, whilst that of V(IV) is performed by sorption onto the second column (C2) filled with mesoporous silica MCM-41 at pH 5. Aqueous samples containing both analytes are loaded and, after pre-concentration (pre-concentration factor PCF = 10, sorption flow rate = 1 mL min⁻¹, sorption time = 10 min), they are eluted in separate vessels with hydroxylammonium chloride (HC) 0.1 mol L⁻¹ in HCl 0.5 mol L⁻¹ (elution volume = 1 mL, elution flow rate = 0.5 mL min⁻¹). Afterwards, both analytes are determined through ETAAS with graphite furnace. Under optimized conditions, the main analytical figures of merit for V(V) and V(IV) are, respectively: detection limits (3 s): 0.5 and 0.6 μg L⁻¹, linear range: 2–100 μg L⁻¹ (both analytes), sensitivity: 0.015 and 0.013 μg⁻¹ L and sample throughput: 6 h⁻¹ (both analytes). Recoveries of both species were assayed in different water samples. Validation was performed through certified reference materials for ultratraces of total vanadium in river water.

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1. Introduction

Vanadium is highly distributed in the Earth's crust and deserves great attention in industrial applications such as those concerning the manufacturing of alloys, glasses, pigments, etc. Particularly, it is present in fossil fuels which release the metal to the environment when it is burnt [1].

Generally, the metals toxicity depends on the oxidation state. Vanadium is present in natural waters in concentrations ranging between 1 × 10⁻⁷ and 5 × 10⁻⁷ mol L⁻¹ [2], being the more relevant species V(V) and V(IV). V(V) is present as VO₂⁺ and VO₄³⁻ in acid and alkaline media, respectively. However, at the above mentioned concentrations and the pH values usually occurring in natural waters, it should be present as H₂VO₄⁻. V(IV) lives as VO²⁺ in a reductive and acid media but it can be oxidized by the atmospheric oxygen.

Considering the low concentrations present in natural waters, it becomes necessary the employment of pre-concentration systems before its determination by UV-vis [3], ICP-OES [4], ET AAS [5], etc. The literature describes several approaches for on-line or off-line vanadium preconcentration employing solid phase extraction (SPE). Gil et al. employed carbon nanotubes after complexation with 1,2-ciclohexandiaminetetraacetic acid for the determination of V(IV) [6]. Polymeric solids holding immobilized ligands are also popular amongst retention materials. Polystyrene-divinylbenzene resins functionalized with 4,5-dicarboxy imidazol have been employed for the simultaneous retention of V(IV) and V(V) followed by sequential elution of both analytes [7]. Other approaches involve the employment of molecular sieves for the retention of the complex between V(IV) and Eriochrome cyanine R followed by the sequential reduction of V(V) into V(IV) for sequential speciation [8], etc. Regarding hybrid mesoporous materials, they have been widely employed for the retention of metals for decontamination purposes [9–11]. Mostly of studies reported in the literature involve off-line determination of organic [12] and inorganic analytes [13–15]. On-line analytical applications are scarce [16–20] probably due to problems related to the inefficient release

* Corresponding author. Tel.: +54 1145763360; fax: +54 1145763341.
E-mail address: tudino@qi.fcen.uba.ar (M.B. Tudino).

of the analytes once sorbed. In the particular case of vanadium, no papers involving either total vanadium determination or analytical speciation at ultratrace levels by retention onto this kind of solids are reported up to date.

In this work, we present a new methodology for the non-chromatographic determination of V(V) and V(IV) by SPE-FI-ETAAS. Lab-made hybrid mesoporous silica functionalized with 3-aminopropyltriethoxy silane (APS) [17,18] and mesoporous silica MCM-41 were employed for the retention of V(V) and V(IV), respectively. A flow injection system holding two microcolumns (MC) set in parallel was designed in order to retain both analytes at a suitable pH onto each one of the fillings, employing just one sample loading. Once retained, the analytes were sequentially eluted by means of a solution with strong redox properties in highly acidic media. Afterwards, both inorganic species were off-line determined by ETAAS.

The advantages of this methodology will be presented in terms of analytical figures of merit. Results involving the determination of V(V) and V(IV) in natural waters and the validation of the analytical methodology will be provided.

2. Experimental

2.1. Reagents

Standard solutions of 1.000 g L^{-1} of V(V) were prepared by dissolving 0.1148 g of ammonium metavanadate (99.9%, Merck Darmstadt, Germany) in 50 mL de double deionized water (DDW) ($18 \text{ M}\Omega \text{ cm}^{-1}$, MilliQ Water System, Millipore, Bedford, MA, USA). 1.000 g L^{-1} of V(IV) standards were prepared by dissolving 0.2484 g of vanadyl sulfate (Merck) in 50 mL of DDW.

$5 \times 10^{-3} \text{ mol L}^{-1}$ ammonia solutions were prepared by a suitable dilution of concentrated NH_3 (Merck). Concentrated HCl (Merck) was employed for preparing solutions at pH 3. The eluent solution was prepared by dissolving 0.6949 g of hydroxylammonium chloride (HC) in 100 mL of HCl 0.5 mol L^{-1} .

Sodium tetraethylorthosilicate (TEOS) 98% ($M_r = 208.33$, $d = 0.934 \text{ g mL}^{-1}$), cetyl trimethylammonium bromide (CTAB) ($M_r = 364.46$) and 3-aminopropyltriethoxysilane (APTES) ($M_r = 221.37$, $d = 0.942$) (Sigma–Aldrich, St Louis, MO, USA) were employed for the synthesis of hybrid 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 DDW, ethanol and acetone.

2.2. Sample treatment

Water samples were previously filtrated through nylon membranes ($0.45 \mu\text{m}$). Afterwards, standard additions of $50 \mu\text{g L}^{-1}$ of both, V(V) and V(IV), were performed in order to test recoveries in real samples.

The reference material (NIST, SRM 1643e, total vanadium certified concentration = $37.86 \pm 0.56 \mu\text{g L}^{-1}$) was diluted 1:2 with DDW and kept at pH 3 by the addition of NaOH (Merck) 1 mol L^{-1} .

2.3. Apparatus

The flow system FI (Fig. 1) was assembled with a peristaltic pump (IPC, Ismatec, Glattbrugg–Zürich, Switzerland), a ten-ports rotatory valve VICI (Valco Instruments, Houston, TX, USA), 0.5 mm i.d. PTFE® tubings (Cole Parmer, Chicago, IL, USA) and two acrylic microcolumns (MC) with the inner part drilled to obtain a $7.9 \mu\text{L}$ bed volume (10 mm long, 1.0 mm internal diameter). Both MC were 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. Two plugs of polystyrene foam were placed at both sides of the MC and the solids were slurry loaded (0.1 g) into the MC with a plastic syringe.

Samples were analyzed by graphite furnace atomic absorption spectrometry (GFAAS) with a Shimadzu graphite furnace atomic absorption spectrometer AA6800 (Shimadzu, Kyoto, Japan) equipped with an autosampler Shimadzu ASC-6100. Vanadium hollow cathode lamp (Hamamatsu, Japan), deuterium lamp background correction and pyrolytic graphite furnaces (platform atomization) were employed throughout the measurements. Instrumental conditions are listed in Table 1a and b.

2.4. Procedure

2.4.1. Synthesis of hybrid mesoporous solids

The solid APS was prepared according to the methodology described by Fowler et al. [19] and previously reported elsewhere [16,17].

2.4.2. Preconcentration and determination of V(V) and V(IV)

Fig. 1 shows the SPE-FI system employed for V(V) and V(IV) preconcentration.

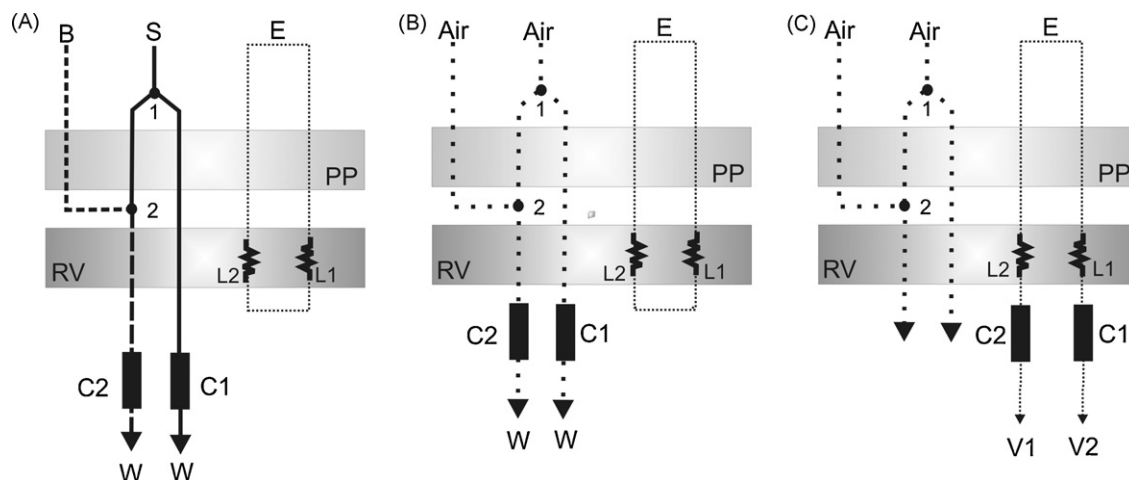


Fig. 1. FI system for vanadium speciation. (a) Sample loading position onto microcolumns C1 and C2. Sample loading flow rate: 1 mL min^{-1} , ammonia solution (B) flow rate: 0.2 mL min^{-1} , waste (W), peristaltic pump (PP), sample (S), ten-ports rotatory valve (RV), eluent solution (E), eluent loops ($L_1 = L_2$), sample bifurcation (1), pH conditioning confluence (2), vessels (V1 and V2). (b) Sample and ammonia streams are emptied before eluent injection. (c) Elution position: elution flow rate: 0.5 mL min^{-1} .

Table 1
Instrumental conditions for total V determination and graphite furnace temperature program.

Parameter				
(a)				
Wavelength	318.5 nm			
Spectral bandpass	0.2 nm			
Lamp current	10 mA			
Background correction	Deuterium lamp			
Sample volume	80 μ L			
Stage	Temperature ($^{\circ}$ C)	Ramp time (s)	Hold time (s)	Argon gas flow (L min $^{-1}$)
(b)				
Drying	120	30	–	1.00
	250	10	–	1.00
Pyrolysis	650	40	–	1.00
	650	–	5	0.00
Atomization	2650	–	2	0.00 (read)
	2650	–	1	0.30

Sample and standard solutions are introduced in the microcolumns C1 and C2 at pH 3 and pH 5, respectively, at 1 mL min $^{-1}$ flow rate and a preconcentration time of 10 min. The confluence carrying 5×10^{-3} mol L $^{-1}$ ammonia solution at 0.2 mL min $^{-1}$ (point 2) allows pH conditioning of the sample when passing through C2 at a total flow rate of 1.2 mL min $^{-1}$ in this MC. Even though C2 is loaded at a higher flow rate than C1, the total mass of each analyte loaded onto C1 and C2 respectively, remains the same. Fig. 1 A shows the FI system in loading position. Whilst the samples are going through the microcolumns, two separate loops (1.0 mL volume, 0.5 mm i.d, 127 cm length) are filled with the eluent which is recycled in a closed circuit.

After 10 min, the sample and ammonia solutions are removed allowing air to enter into the flow system lines (Fig. 1B). Once all lines are filled with air, the valve is commutated and the elution loops are emptied by a simple air displacement. Thus, the solution containing hydroxylammonium chloride (HC) 0.1 mol L $^{-1}$ in HCl 0.5 mol L $^{-1}$ (elution volume = 1 mL, flow rate = 0.5 mL min $^{-1}$) is carried towards both MCs, allowing the release of V(V) from C1 and V(IV) from C2. Eluates are collected in separate vessels and measured off-line by ETAAS (Fig. 1C).

2.4.3. Adsorption kinetic studies of V(V) and V(IV)

Batch experiments were performed by suspending 500 mL of solutions 5 mg L $^{-1}$ of V(V) and V(IV) in 100 mg of APS. Measurements were carried out by taking 100 μ L aliquots of the supernatant at different times of contact between the analyte and the filling.

3. Results and discussion

3.1. Optimization of pH for sorption of V(V) and V(IV)

Several batch experiments were conducted with the aim of evaluating the influence of pH on the sorption of V(V) and V(IV) onto APS. HCl or NaOH solutions were employed for pH conditioning. For doing this, 500 μ g L $^{-1}$ solutions of V(V) and V(IV) in separate vessels were contacted with APS at pH values ranging between 1 and 9. Suspensions were agitated during 24 h and then centrifugated at 3200 rpm. Remaining vanadium was measured in the supernatant solution by ETAAS.

Fig. 2 shows the sorption behaviour of both forms of vanadium vs. pH.

The maximum adsorption capacities q (mmol g $^{-1}$) of V(V) and V(IV) were observed at pH 5, being q lower for the latter. At pH 5 and concentrations below 10^{-6} mol L $^{-1}$, V(V) is present as H_2VO_4^- whilst the net surface charge of APS is positive. In this way, it is retained by electrostatic interaction with the filling. At lower pH, sorption capacity diminishes due to the protonation of V(V) which lives as the cationic form VO_2^+ [20] whilst the net surface charge of APS is still positive. At pH above 5, V(V) remains in the anionic form and q decreases mainly because the surface charge of silica is negative and the aminopropyl groups are now not charged. Since the most remarkable difference of sorption capacities was observed at pH 3, it was selected for conditioning of C1.

For pH values between 0 and 5, V(IV) is mostly present as VO^{2+} and $(\text{VO})_2(\text{OH})_2^{2+}$. In this pH range, the net surface charge of the solid changes from positive (pH < 2) to negative with not charged aminopropyl groups for pH above 5. So, the larger the net negative charge of the surface, the higher the absorption of V(IV) by electrostatic interaction with the filling. The decrease of q at higher pH values is attributed to the precipitation of oxo-hydroxo species with a general formula $\text{VO}_2 \cdot n\text{H}_2\text{O}$ ($K_{\text{ps}} \approx 10^{-22}$). In extremely basic conditions, the anionic form $\text{VO}(\text{OH})_3^-$ is obtained and thus, the oxo-hydroxo species solubilized [20].

The same experiments were carried out in order to study the influence of pH on the adsorption of both analytes onto silica MCM-41 (Fig. 3). In this case, the filling achieves net charge zero (at low pH) or negative charge (pH 2 or above) and still, some retention of V(V) species was observed. In the case of V(IV), the positive charged species showed larger q values when raising pH up to 5–6. From 6 onwards, the analyte precipitates as told above. So, pH 5 was selected for conditioning C2. However, the aptitude of MCM 41 for specific retention of V(IV) seemed not enough for its determination with no interference of V(V) through batch operations.

In this way, flow through experiments were assayed in order to reach specificity by kinetic discrimination. The same experiments were carried out on line by simply passing through the flow sys-

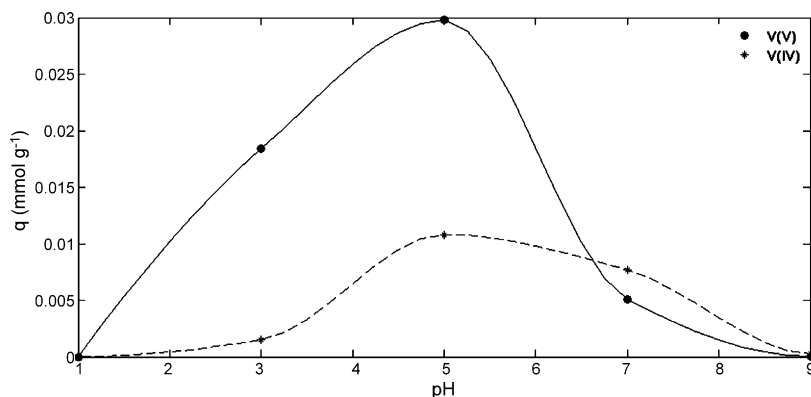


Fig. 2. Influence of pH on the retention of V(V) and V(IV) onto APS (batch). [V(V)]: 500 μ g L $^{-1}$, [V(IV)]: 500 μ g L $^{-1}$.

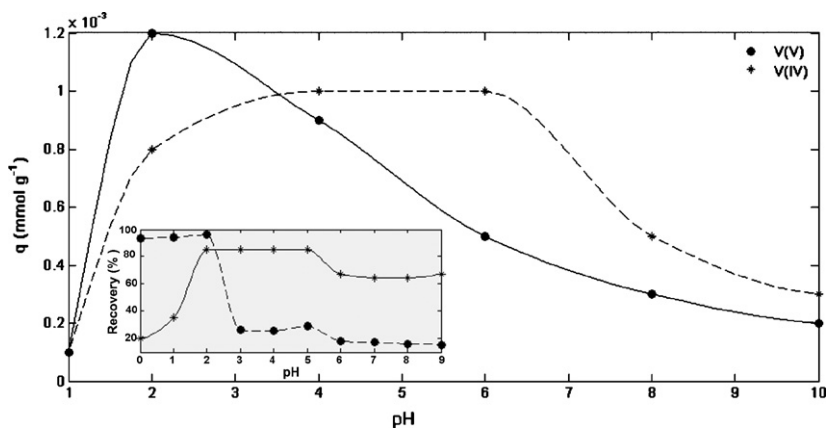


Fig. 3. Influence of pH on the retention of V(V) and V(IV) onto MCM-41 (batch). [V(V)]: $500 \mu\text{g L}^{-1}$, [V(IV)]: $500 \mu\text{g L}^{-1}$. Inset: flow through experiments.

tem, solutions of V(V) and V(IV) $50 \mu\text{g L}^{-1}$ with a preconcentration factor ($\text{PCF} = V_{\text{sample}}/V_{\text{eluent}} = 10$, adsorption flow rate = 1 mL min^{-1} and elution flow rate = 0.5 mL min^{-1}). The findings obtained under flow through conditions and thus, the influence of the adsorption kinetics on the determination of both analytes with no mutual interference, will be discussed in the next section.

3.2. Influence of the adsorption flow rate on the retention of V(V) and V(IV) and kinetic studies

It was observed that the percentages of recovery remained relatively constant and equal to 95% for V(V) onto C1 and 85% for V(IV) onto C2 up to 1 mL min^{-1} loading flow rate (Fig. 4a and b). The adsorptions of V(IV) onto C1 and V(V) onto C2 were neglectable. Note that, whilst the specificity on V(V) retention onto APS was obtained by pH discrimination, the specificity on V(IV) sorption onto MCM-41 was only obtained under flow through conditions. This last circumstance should be assigned to a remarkable difference between adsorption kinetics of both analytes onto MCM-41 under the experimental conditions: a contact time of about 0.4 s. Neither filling compactation nor pressure enhancement were observed for this flow rate value. Loading flow rate of 1 mL min^{-1} was selected in order to optimize the sample throughput without enlarging the time of preconcentration. In order to keep PCF constant and equal to 10, the loaded mass of the analytes was kept constant along the experiments. Taking into account that the adsorption kinetics influence the specificity, the effect of the loading flow rate on the retention of V(V) and V(IV) onto both fillings at the optimized pHs, were carried out. Fittings of experimental data were calculated by the Pseudo Second order

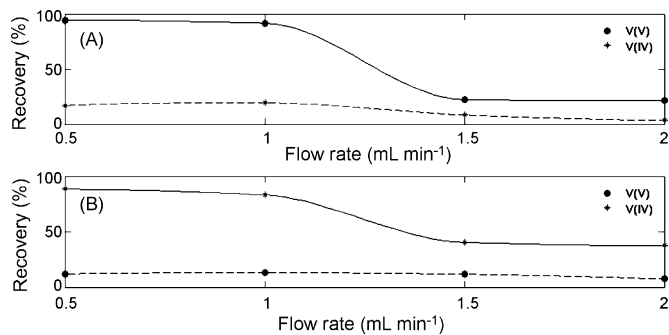


Fig. 4. (a and b) Influence of the flow rate on: (a) the adsorption of V(V) and V(IV) onto APS (C1) at pH 3 and (b) the adsorption of V(V) and V(IV) onto MCM-41 (C2) at pH 5. [V(V)] and [V(IV)] = $30 \mu\text{g L}^{-1}$, elution flow rate: 0.5 mL min^{-1} , elution volume: 1 mL, PCF = 10.

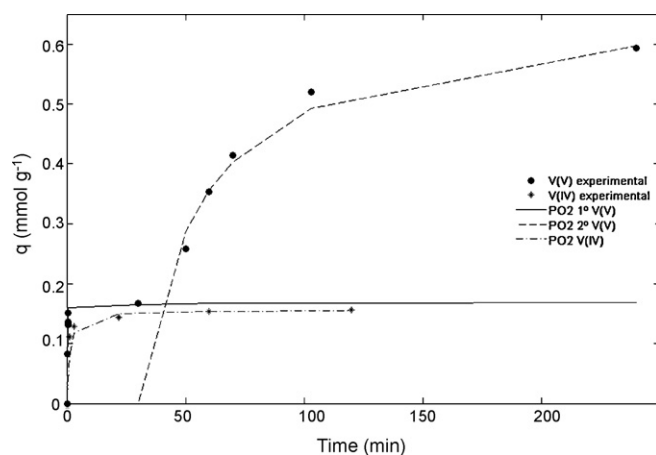


Fig. 5. Adsorption kinetics of V(V) and V(IV) onto APS at pH 3. [V(V)] = [V(IV)] = 5 mg L^{-1} . APS = 100 mg (slurry loaded onto C1). Experimental and calculated data (PO2 kinetic model). V(IV) experimental and calculated data are 100 times enhanced in order to keep the same scale.

kinetic model (PO2) [21–23] which showed the best correlation.

The figures show that the adsorption kinetic curves of V(V) and V(IV) at pH 3 onto APS20% (Fig. 5) are significantly different from those onto MCM-41 at pH 5 (Fig. 6). Fig. 5 shows two well differentiated steps: a first plateau up to 50 min and a second one up to 300 min where two q_{max} values are obtained. This circumstance should probably be related to the existence of two predominant species of V(V), VO_2^+ and H_2VO_4^- ($\log K = 2.6$) [20], that interact differently with the solid at pH 3. Under these conditions, the

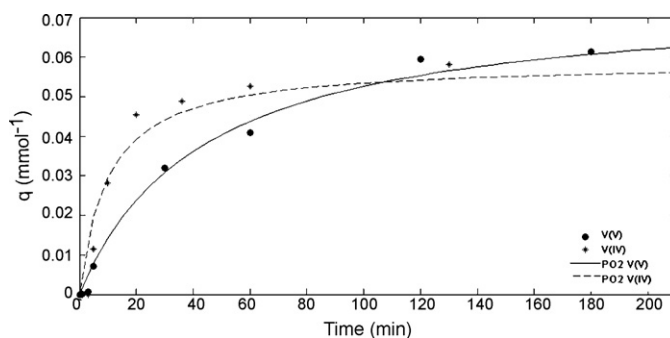


Fig. 6. Experimental and calculated data (PO2 kinetic model) for adsorption kinetics of V(V) and V(IV) onto MCM-41 at pH 5. [V(V)] = [V(IV)] = 5 mg L^{-1} . MCM-41 = 100 mg (slurry loaded onto C2).

silanols deprotonation should be responsible for the first portion of the curve corresponding to the electrostatic interaction of VO_2^+ with the negatively charged silanols [2]. The second part should be attributed to the interaction of H_2VO_4^- with the positively charged aminopropyl groups. This should be the reason why two different approaches were needed for explaining the whole response: PO2 1° for 0–50 min and PO2 2° for 50 min onwards. At pH 5 (Fig. 6), H_2VO_4^- is the predominant specie of V(V) so, the q vs. t plot shows only one step corresponding to the adsorption of negatively charged V(V) onto MCM-41. In the case of V(IV) no differences on the shape of the adsorption kinetic curves were observed. This should be explained by taking into account that, as said above, V(IV) is present as VO^{2+} and/or $(\text{VO})_2(\text{OH})_2^{2+}$ and thus, no different adsorption behaviors onto the negative surface charge of the solid should be expected. Thus, only one step kinetic curve is observed, and just one fitting is needed. Note that, at the selected contact times between both analytes and MCM-41 the adsorption of V(V) is now unimportant due to the differences of the initial adsorption rates ($V_{\text{V(IV)}}^0 = 3 V_{\text{V(V)}}^0$).

Flow through studies were carried out in order to re-evaluate the influence of pH onto adsorption capacities when kinetic discrimination is taken into account. Experiments involving adsorption of V(V) and V(IV) onto APS showed no significant differences with respect to the findings in Fig. 2. Regarding the flow through behavior onto MCM-41, adsorption was seriously affected by the time of contact analyte/filling, allowing in these way, V(IV) retention with no interference of V(V) (Fig. 3 inset).

3.3. Studies on the optimum preconcentration factor

The variation of PCF was achieved keeping the adsorption flow rate constant and changing the preconcentration time. As shown in Fig. 7, recoveries of V(V) and V(IV) remain practically constant and around 95% and 85% respectively, up to PCF = 10. Above this, a decrease is noticed with PCF values close to 60% and 50% for V(V) and V(IV) respectively.

3.4. Influence of the eluent characteristics on the analytes recoveries

Several solutions were assayed in order to accomplish an efficient release of V(V) and V(IV) by employing low volumes of an ETAAS friendly eluent. On the belief that changes in pH and redox environment should produce good liberation of the analytes by species conversions, the solutions listed in Table 2 were tested in terms of percentage of recovery of V(V) and V(IV).

Even though E2 and E5 showed the best performance for V(V) elution, E2 was preferred considering that the nitric acid in E5 should probably oxidize APS, reducing in this way the filling life-time. In order to prevent oxidation of the filling, E5 in HCl [16] was

Table 2

Eluents for V(V) and V(IV), sorbed onto C1 and C2, respectively. $[\text{V(V)}] = [\text{V(IV)}] = 50 \mu\text{g L}^{-1}$, elution flow rate: 0.5 mL min^{-1} , eluent volume: 1 mL, adsorption flow rate: 1 mL min^{-1} , PCF: 10.

Eluent	Eluent solution	Recovery V(V) (%)	Recovery V(IV) (%)
E1	HCl 1 mol L^{-1}	69.2	100
E2	HC 0.1 mol L^{-1} + HCl 1 mol L^{-1}	91.8	99
E3	HNO_3 1 mol L^{-1}	42.6	98
E4	Ascorbic acid 1%w/v	29.1	56
E5	1,5-Diphenylcarbazide in $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ [24]	99.1	100

also tested but a relatively high background signal in the detector was observed even when the time of pyrolysis was enlarged. It was also observed that changes of pH were not enough to release efficiently V(V) and that changes of the redox properties (conversion of the negatively charged H_2VO_4^- into the cation VO^{2+}) were also needed.

V(IV) was completely recovered under strong acid conditions showing that the release is possible by simply changing the surface charge of MCM-41. E2 was also selected in order to employ the same eluent for both species, making simpler the flow manifold design. It was found that HC 0.1 mol L^{-1} in HCl 0.5 mol L^{-1} was optimum for 100% elution of V(V) and V(IV). Moreover, E2 was an excellent solvent for ETAAS as HC easily decomposes into the graphite furnace.

3.5. Elution volume

In order to obtain the best PCF together with the use of the minimum volume of reagents and the production of the minimum volume of waste, the eluent volume was optimized by changing the dimensions of the eluent loops of the flow system (see Fig. 1) and keeping constant the adsorption flow rate and the elution flow rate. Results for V(V) and V(IV) recoveries are shown in Fig. 8.

A 95% V(V) and 85% V(IV) recovery was obtained for 1 mL onwards for both analytes and this value was selected as optimum. Note that lower volumes showed a poor response which obliged us to off-line injection into the GF which handles upmost $100 \mu\text{L}$ (sample injected volume: $80 \mu\text{L}$).

3.6. Optimization of the elution flow rate

Fig. 9 shows the influence of elution flow rate on the analytes release, keeping constant the eluent volume. Best results were obtained for 0.5 mL min^{-1} or below. Again, it was observed that the times of contact between the analytes and the fillings and those of the analytes and the eluent determine the efficiency of the whole analytical procedure. As told before, the adsorption kinetic is slow

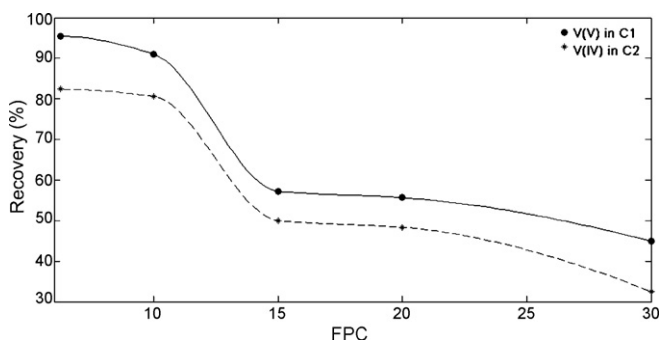


Fig. 7. Optimum preconcentration factor (PCF) for V(V) in C1 and V(IV) in C2. $[\text{V(V)}] = [\text{V(IV)}] = 50 \mu\text{g L}^{-1}$ pH 3 in C1 and pH 5 in C2, adsorption flow rate: 1 mL min^{-1} , elution flow rate: 0.5 mL min^{-1} , eluent volume: 1 mL.

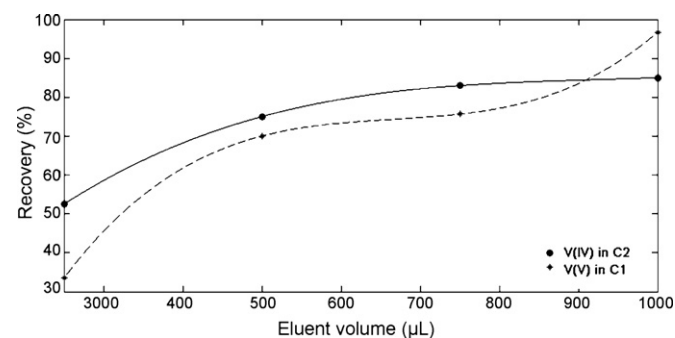


Fig. 8. Optimization of the eluent volume. $[\text{V(V)}] = [\text{V(IV)}] = 50 \mu\text{g L}^{-1}$, eluent flow rate: 0.5 mL min^{-1} , adsorption flow rate: 1 mL min^{-1} , PCF: 10, eluent: E2.

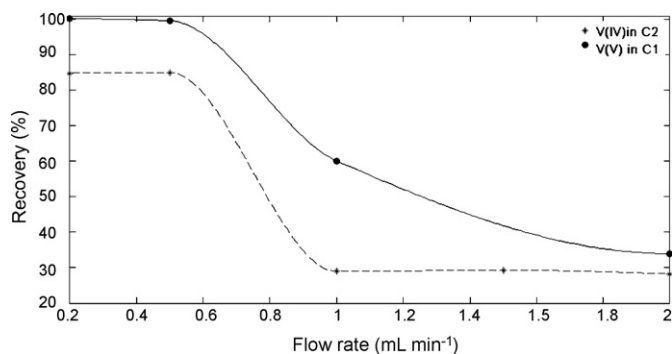


Fig. 9. Influence of the elution flow rate on the recovery of vanadium. $[V(V)] = [V(IV)] = 50 \mu\text{g L}^{-1}$, adsorption flow rate: 1 mL min^{-1} , PCF: 10, eluent: E2, eluent volume: $1000 \mu\text{L}$.

Table 3

MTL of interferences for the determination of V(V) and V(IV).

Interferences	MTL for V(V) determination ($\mu\text{g L}^{-1}$)	MTL for V(IV) determination ($\mu\text{g L}^{-1}$)
Cr (VI)	>100	>100
Fe (III)	>1000	>100
Al (III)	>100	>100
Zn (II)	>100	>100
Cu (II)	>200	>20
Mg (II)	>50,000	>50,000
Ca (II)	>50,000	>50,000
Na (I)	>100,000	>100,000
Cl ⁻	>50,000	>350,000
SO ₄ ²⁻	>100,000	>500,000
NO ₃ ⁻	>100,000	>200,000
PO ₄ ³⁻	>50,000	>200,000

$[V(V)] = [V(IV)] = 50 \mu\text{g L}^{-1}$.

but, once sorbed, the interaction between the analytes and the filling is strong (even stronger for V(V) onto APS). In this way, elution needs to enlarge the times of contact analytes/E2 in order to free them from the solids.

3.7. Influence of interferences

Table 3 shows the influence (expressed as maximum tolerable limit, MTL) of different ions usually present in real water samples, on V(V) and V(IV) analytical signal. It shows that MTLs in C2 at pH 5 (V(IV) determination) are higher for anions which is compatible with the negative surface charge of the filling. On the other hand, MTLs in C1 at pH 3 (V(V) determination) are equal or higher for cations when compared to C2, which is consistent with the positive charge of APS. Regarding Cr(V), an important decrease on V(V) signal is observed probably due to the presence

of HCrO_4^- as predominant specie which competes with HVO_4^- for sorption onto the filling [18]. Table 3 also shows the great tolerance to a high concentration of concomitant ions of the system, which enhances the probability of good vanadium quantification in real samples.

3.8. Analytical figures of merit

Under optimized conditions (adsorption flow rate = 1 mL min^{-1} , elution flow rate = 0.5 mL min^{-1} , $\text{pH}_{\text{C1}} = 3$, $\text{pH}_{\text{C2}} = 5$, elution volume = $1000 \mu\text{L}$, preconcentration time = 10 min) an PCF of 10 with a preconcentration efficiency of 95% of V(V) and 85% of V(IV) was obtained. Detection limits (calculated as $3S_b$) were 0.5 and $0.6 \mu\text{g L}^{-1}$ for V(V) and V(IV), respectively. The characteristic masses were 23 pg for V(V) and 25 pg for V(IV). The relevant figures of merit in comparison to others already reported are listed in Table 4.

Even though the analytical methodologies reported by Aureli et al. [25] and Gil et al. [6] show better limits of detection (other figures of merit are barely shown), two main advantages should be addressed with this proposal: a lower cost of equipment (in comparison to the approach in [25] and a much more simpler pretreatment (in comparison with the approaches in [25] and [6]). Moreover, in comparison with the results in [25], vanadium speciation instead of total vanadium determination is performed here. To enhance: V(V) and V(IV) determination is simply performed by changing the chemical environment (redox potential and pH) during flow through experiments of preconcentration and elution of both forms, with no need of chromatographic separations which usually enlarge the analytical frequency.

3.9. Vanadium determination in real samples

In order to study the matrix effect on V(V) and V(IV) recoveries in real samples, DDW, osmosis, mineral and tap waters were spiked with $50 \mu\text{g L}^{-1}$ of each one of the analytes. The percentages of recovery obtained for the assayed samples are shown in Table 5.

Good results, within the experimental error allowed for ultra-trace analysis, were obtained for both analytes. In the case of V(IV), the standard addition methodology should be applied if more accurate and precise results were needed. The determination of total vanadium in a certified reference material (NIST, SRM 1643e) was also performed by employing the standard addition methodology. The total vanadium content was simply obtained through the sum of the individual concentrations of V(V) and V(IV). The total vanadium concentration was equal to $(38.7 \pm 0.5) \mu\text{g L}^{-1}$ which is in good agreement with the certified value of $(37.63 \pm 0.44) \mu\text{g L}^{-1}$ (95% confidence level, $n = 3$).

Table 4

Comparison of analytical performance of the proposed methodology with data taken from bibliography or others already reported.

Analytical performance	Proposed methodology FI-SPE-ETAAS		ETAAS ^a	HPLC-ICP MS [25]		FI-SPE ETAAS [6]	
	V(V)	V(IV)	Total V	V(IV)	V(V)	V(IV)	V(V)
Speciation	Yes	No	Yes	Yes			
LOD ($\mu\text{g L}^{-1}$)	0.5	0.6	3.5	0.16	0.025	0.019	
Regression equation	$0.015C + 0.006$	$0.013C + 0.004$	$0.0024C + 0.0007$	NR	NR		
Sensitivity ($\mu\text{g}^{-1} \text{L}$)	0.015	0.013	0.0024	NR	NR		
Dynamic range ($\mu\text{g L}^{-1}$)	2–100	2–100	10–600	0.16–16	0.025–50	NR	
Maximum PCF	10	10	–	NR	NR	900	
RSD % ($n = 5$, $50 \mu\text{g L}^{-1}$)	1.8	2.3	3	5.5	1.4	2	
Characteristic mass (pg)	23	25	145	–	–	63000	
Sample throughput (h^{-1})	6	6	30	2	2	20	
Column lifetime (sorption/desorption cycles)	200	200	–	–	–	50	

NR: not reported.

^a Measured in our laboratory.

Table 5
Studies of recovery of V(V) and V(IV) in different water samples spiked with 50 $\mu\text{g L}^{-1}$ of each analyte ($n = 3$, 95% confidence level).

Sample	Added ($\mu\text{g L}^{-1}$)		Found ($\mu\text{g L}^{-1}$)		Recovery (%)	
	V(V)	V(V)	V(VI)	V(IV)	V(V)	V(IV)
DDW	0	0	0.0 \pm 0.1	0.0 \pm 0.6	0	0
	50	50	48.5 \pm 1.8	40.1 \pm 3.1	97	80
Osmosis water	0	0	0.0 \pm 0.1	0.0 \pm 0.1	0	0
	50	50	47.5 \pm 2.1	39.1 \pm 4.2	95	78
Mineral water	0	0	0.0 \pm 0.1	0.0 \pm 0.1	0	0
	50	50	48.5 \pm 2.7	36.2 \pm 3.4	94	72
Tap water	0	0	0.0 \pm 0.9	0.0 \pm 0.1	0	0
	50	50	47.6 \pm 2.7	38.4 \pm 4.3	95	77

4. Conclusions

A simple and reliable methodology for the inorganic speciation of vanadium was developed. The non-chromatographic method, based on sorption of V(V) and V(IV) onto a lab-made hybrid mesoporous solid (silica based), is presented here for the first time. The method requires just one sample loading and just one eluent solution for performing both determinations, making easier the analyst work.

The dual column FI-SPE-ETAAS system showed an excellent performance at the moment of the determination of both forms of vanadium in water samples, even under high ionic strength conditions.

So, the lab-made hybrid mesoporous solids look promising for analytical determinations if their unquestionable sorption capacities [26,27] are combined with: (a) kinetic discrimination schemes for selectivity enhancement [28] and (b) the choice of suitable eluents able to easily liberate the retained analytes by changing the physico-chemical environment of sorption. In this way, the experiments presented here in order to study the adsorption kinetic of both analytes onto the solid materials and their desorption kinetics, should help on advancing in new analytical applications.

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