



In situ determination of V(V) by diffusive gradients in thin films and inductively coupled plasma mass spectrometry techniques using amberlite IRA-410 resin as a binding layer



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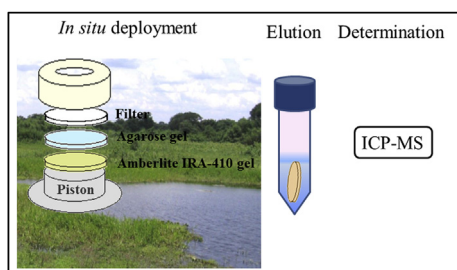
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HIGHLIGHTS

- A new DGT method for sampling V(V) *in situ* was developed.
- For the first time, Amberlite IRA-410 was used as binding layer for V(V) sampling by DGT.
- The diffusion coefficient of V(V) through agarose gel is reported.
- The method was efficient to overcome interference of Cl⁻ in V determination by ICP-MS.
- The proposed approach was efficient to determine V in river and acid drainage water.

GRAPHICAL ABSTRACT



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ABSTRACT

Amberlite IRA-410 anionic exchange resin was evaluated as the binding layer for sampling V(V) by using Diffusive Gradients in Thin Films (DGT). V(V) was determined by inductively coupled plasma mass spectrometry (ICP-MS). Mass vs. time DGT deployments (ionic strength = 0.03 mol L⁻¹ NaNO₃, pH = 5.6 and T = 23.5 ± 0.5 °C) was characterized by excellent linear relationship (R² = 0.9993) and a significant retention of V(V) by the binding layer. An exchange capacity of at least 40 μg V g⁻¹ resin was achieved for the proposed binding layer. The diffusion coefficient obtained (7.13 ± 0.6 10⁻⁶ cm² s⁻¹) agrees with the literature. The accumulation rate of V(V) was not significantly affected by ionic strength of solutions up to 0.03 mol L⁻¹ and for the entire studied pH range (from 3 to 9). Furthermore, when comparing the concentrations obtained using IRA-410-DGT and those obtained by direct measurement of the solution concentrations, the proposed approach provided a reduction of the ³⁵Cl¹⁶O interference on V(V) determination by ICP-MS. Determination of V in normal mode (without collision cell) in solutions containing analyte:Cl⁻ concentration ratio up to 1:500,000 was not affected by interference of ³⁵Cl¹⁶O⁺ polyatomic ion even when normal mode ICP-MS was used. Potential interfering ions on sampling V(V) by DGT (PO₄³⁻ and SO₄²⁻) showed no significant effects on the accumulation rate of V(V). Laboratory tests performed using synthetic samples, natural freshwater and acid drainage water showed an excellent performance

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(recoveries from 93% to 110%). For *in situ* deployment, measurements of V(V) by the proposed approach was not significantly different (95.5%) from the value of dissolved V concentration.

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1. Introduction

The abundance of V in nature is 0.0014%, evenly distributed with few high concentration depots [1]. Natural V occurrence is mainly due to marine spray, volcanic activity and parental rock leaching, while fuel combustion (coal and oil) accounts for the anthropogenic sources [2]. The major part of V used for industrial purposes is obtained from titanomagnetite, which holds 0.8% of the element [3]. The primary route of environmental contamination by V is the emission of particulate matter to the atmosphere, which is then carried to soil and oceans as well as other water bodies [4]. Monitoring V concentrations has been successfully proposed to assess the pollution impact on a neighborhood of an industrial installation [5] and impact of oil spills [6,7].

Due to its similarity to PO_4^{3-} , V oxyanions have been reported as interfering in the activity of PO_4^{3-} dependent enzymes in biological systems [8] (i.e. ATPases). Previous studies and references therein have reported beneficial or adverse effects on organisms exposed to V depending on the exposure concentration [9,10] which highlights the importance of monitoring this metal.

Since V presents low concentrations under natural conditions, it is important to develop an efficient sampling method capable of pre-concentrating this metal, as well as to provide its determination by an analytical technique that enables its quantification at very low detection limits, such as inductively coupled plasma mass spectrometry (ICP-MS). However, the use of quadrupole ICP-MS (Q-ICP-MS) for determination of V is subject to spectral interferences, mainly for samples rich in Cl^- , wherein the occurrence of the polyatomic ion $^{35}\text{Cl}^{16}\text{O}^+$ interferes on ^{51}V measurements (the most abundant isotope of the element). Although a collision cell can be used to overcome this interference, its use results in a significant increase of detection limit of V [11].

Diffusion gradients in thin films technique (DGT) was proposed in 1994, for passive *in situ* sampling of labile metals by the deployment of a device in aquatic systems. Besides its simplicity, other convenient DGT attributes are the possibility of maintaining the oxidation state of the studied species, pre-concentration of analytes, multielement sampling and providing the average concentration of water bodies which may vary markedly over time [12].

Österlund et al. [13] investigated the efficiency of ferrihydrite (backed) immobilized on polyacrylamide gel as DGT binding agent for sampling V(V) ion, along with other four oxyanions in freshwater. *In situ* performance suggests that the proposed method is efficient to sample V(V).

Luo et al. [14] studied the performance of ferrihydrite for the determination of As(V), Se(VI), V(V), and Sb(V) in synthetic solutions. The binding discs were prepared in an unconventional way (precipitated ferrihydrite). By using the new approach, a lower limit of detection was obtained, having also achieved greater exchange capacity due to greater surface of iron hydroxide.

Panther et al. [15] evaluated the titanium dioxide (Metsorb^(TM)) binding layer for sampling V(V) along with other anions in fresh and sea waters by Q-ICP-MS. The method works properly for freshwater and, for synthetic sea waters, Metsorb^(TM) performance was satisfactory for the studied period of four days.

Zirconium oxide was successfully proposed as a binding phase

to sample V(V) and other six oxyanions by DGT in water and sediment. The method was considered much more efficient when compared to the other two previously proposed, because it has higher exchange capacity and is more tolerant to interfering ions, additionally to working properly in waters of the same range of pH and ionic strength [16].

Price et al. [17] compared ferrihydrite and Metsorb^(TM) for DGT sampling of V(V) and other anions. The authors considered the binding layers to behave very similarly in freshwaters and suggested an optimization for both in order to achieve a better exchange capacity, which is especially relevant to marine water deployments.

In waters of oxygenated conditions, V(V) is expected to be the prevailing form, being present as an oxyanion in pH close to neutrality and basic (H_2VO_4^- , HVO_4^{2-} and VO_4^{3-}) and cationic in acid conditions (VO_2^+). Also, V(IV) and V(III) are expected to be present as cations in natural waters [18]. As V(V) is more soluble than the other oxidation states [19], it is expected to be the predominant dissolved species in natural waters. Therefore, Amberlite IRA-410, as a strongly basic anionic resin, is expected to be selective to V(V) in natural waters.

The main aim of this work was to develop a method for determining V(V) at low concentrations (sub ng mL^{-1}) reliable for a wide range of freshwaters. In this paper, we pursuit to accomplish it by using DGT devices assembled with Amberlite IRA-410 coupled with ICP-MS. Additionally to pre-concentrating V(V) in water samples, we focus on a binding layer able to pre-concentrate V(V) more efficiently than Cl^- in order to overcome $^{35}\text{Cl}^{16}\text{O}^+$ interference on measurements by Q-ICP-MS without the use of instrumental approaches.

2. Experimental

2.1. DGT theory

By using a diffusive gel, commonly polyacrylamide, an ion is transported into a binding phase exclusively by molecular diffusion, thus Fick's First law can be used for the calculation of the concentration of the ion in solution. Therefore, concentration of the bulk solution can be determined by Eq. (1) [20]:

$$C_b = (M \Delta g) (D t A)^{-1} \quad (1)$$

where C_b is the bulk solution concentration (ng mL^{-1}); M is the analyte mass (ng) retained by the binding layer; Δg (cm) is the thickness of the diffusive layer; D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of the ion in the diffusive medium; t is time (sec); and A (cm^2) is the area of the layers exposed to the solution.

The mass of the accumulated ion is obtained by eluting it from the binding layer and then determining the concentration of the eluate (C_e , ng mL^{-1}) by a suitable analytical technique.

$$M = C_e (V_{ac} + V_b) F_E^{-1} \quad (2)$$

where:

V_{ac} = acid volume (mL) used in the elution

V_b = volume (mL) of the binding layer discs
 F_E = elution factor

2.2. Equipment and material

Concentration of V(V) was determined by Inductively coupled plasma mass spectrometer X-Series 2 (Thermo Scientific, Germany), equipped with a Mira Mist[®] nebulizer (Burgener research Inc, Canada) and Thermo spray chamber at 4 °C or, alternatively by Inductively Coupled Plasma Optical Emission Spectrometer Icap 6300 (Thermo Scientific), equipped with V Grove nebulizer (Glass Expansion, Australia) and cyclonic spray chamber (Glass Expansion). The ICP OES operation conditions were optimized as specified by the manufacturer. Determination of V by ICP-MS was carried out at m/z 51 on normal mode (without reaction cell and kinetic energy discrimination).

Conductivity was obtained by Jenway conductivity Meter (model 470, UK) and pH was measured by Jenway pH Meter (model 3505). DGT devices (polypropylene piston and cap) were purchased from DGT Research Ltd, Lancaster, UK.

2.3. Reagents and solutions

All reagents used were of analytical grade. Solutions were prepared with ultrapure water with a resistivity of 18 M Ω cm⁻¹ (Milli-Q, Millipore Academic, USA). HNO₃ (Merck, Germany) was distilled off below the boiling point for greater purity (Distillacid, Berghof, Germany). NaNO₃ (Merck) was used to adjust the ionic strength (I). HNO₃ and NaOH (Merck) were used to adjust pH.

Ammonium metavanadate (Fluka Chemika, Switzerland) was used to prepare V(V) stock solution of 440 mg L⁻¹ by the dissolution of the salt in ultrapure water. To avoid the adsorption of metals on container surface, it is recommended the acidification of the samples (pH < 2). However, this acidification could disturb the balance of the V species present in the solution [21]. According to Okamura et al. [22], a V(V) solution prepared with ultrapure water, remained stable in the pH range of 2–9, throughout all the investigated period (24 h). Thus, the V(V) stock-solution was kept refrigerated in closed bottle and no acidifying procedure was performed. In all tests, the concentration of V(V) in stock-solution was checked using a multielement standard solution ICP-G2V 100 mg L⁻¹ (SpecSol, Brazil), traceable to NIST-USA.

NaH₂PO₄·H₂O and Na₂SO₄ were used to prepare working solutions for the evaluation of interfering ions test.

Strongly basic anion exchange Amberlite IRA-410 resin in its chloride form was obtained for the binding gel preparation (Aldrich, EUA) and biotechnology grade agarose was purchased from Amresco (Solon, USA) for manufacturing agarose diffusive gels. Polyacrylamide gel was replaced by agarose gel because they have quite similar behavior regarding diffusive coefficient (1.10 times values reported for polyacrylamide gels), handling and storage [23], additionally to agarose providing an easier immobilization for the binding layer.

Prior to using, all working material were immersed in a 20% (v/v) HNO₃ solution for 4 h, rinsed with deionized and ultrapure water to eliminate HNO₃ residues and allowed to air dry.

2.3.1. Cellulose acetate filter

Cellulose acetate membrane (2.5 cm diameter discs, 0.45 μ m pore size and thickness from 115 to 145 μ m) was obtained from Sartorius (Germany).

For decontamination, these discs were immersed in 10% (v/v) HNO₃ solution for 12 h, and then rinsed with ultrapure water until the pH of the washing solution was greater than 5. The

decontaminated discs were stored in refrigerator, in closed flasks containing ultrapure water.

2.3.2. Diffusive layer preparation

Agarose diffusive discs 1.5% (w/v) were obtained by weighting 0.30 g of agarose and adding 20 mL of ultrapure water. Then the mixture was heated under stirring for homogenization. The solution was injected, with the aid of a syringe between two glass plates separated by a spacer 0.8 mm thick. After 40 min, a solidified gel was obtained and it was cut into 2.5 cm discs, which were stored in refrigerator in flasks containing ultrapure water. For at least 24 h prior to use, the discs were immersed in 0.03 mol L⁻¹ NaNO₃ solution.

2.3.3. Binding gel discs preparation and DGT assembly

Amberlite IRA-410 is a strongly basic anion exchange resin commercialized in Cl⁻ form. To increase the surface contact of the functional group to the solution, it was submitted to the micro-metric grinding in a ball mill (MLW – model KM1, Germany) and then the granules between 140 μ m and 250 μ m were selected.

The resin was treated with 10% (v/v) HNO₃ for 4 h under stirring, to change the counter-ion from Cl⁻ to NO₃⁻. Thus, Cl⁻ concentration in the eluate is expected to be reduced and the interference in V determination by ICP-MS is consequently minimized. Then, the resin was rinsed until the pH of purified water and oven dried at 40 °C to avoid possible changes in the resin structure as recommended by manufacturer.

The first immobilization of Amberlite IRA-410 was carried out using agarose 1.5% (w/v) gel. However, to ease the homogenous distribution of the resin on the plates, agarose 3.0% (w/v) was found to be better.

The resin was immobilized on agarose 3.0%, at a ratio of 2.00 g of Amberlite IRA-410 for 10 mL agarose, which was prepared by weighting 0.30 g of agarose and adding 10 mL ultrapure water under stirring and heating. The mixture was poured between two glass sheets separated by a spacer. The glass plates were preheated to ease the uniform insertion of the solution. After 40 min, the obtained gel was cut into 2.5 cm discs (0.4 mm thick) which were stored in flasks containing ultrapure water in the refrigerator.

To assemble the devices, the layers were added over the polypropylene piston in the following order: one Amberlite IRA-410 immobilized on 3% agarose (w/v) disc, followed by 1.5% (w/v) agarose disc and a cellulose acetate membrane disc on the top.

2.4. Accumulation rate of V(V) by the Amberlite IRA-410 disc and elution factor (solid phase extraction using Amberlite IRA-410 discs)

Four V(V) standard solutions were prepared (5, 20, 50 and 100 ng mL⁻¹, duplicate for each concentration) in 50 mL Falcon tubes (I = 0.03 mol L⁻¹ NaNO₃ and pH = 5.6 \pm 0.1 with NaOH). The stirred solutions were allowed to equilibrate for 24 h prior to the deployment. Thus, possible metal adsorption to the tube walls would occur in this period, avoiding analyte losses during immersion. An Amberlite IRA-410 disc was immersed in each tube, which remained under stirring for six hours. Before the immersion of the discs and after their retrieval, an aliquot was collected from each solution. After this period, V(V) elution from discs was performed as described below in Elution (item 2.5). Concentration of V(V) in the eluates was obtained by ICP OES.

By the difference between the mass of V(V) in the initial and final aliquots, the V(V) retained mass in each disc was obtained (M_r). M_e was obtained from the concentration of V(V) in the eluate of the respective disc.

The elution factor was calculated as follows:

$$F_E = M_e M_r^{-1} \quad (3)$$

2.5. Elution

In this work, the elution procedure was carried out using 3 mL of 1 mol L⁻¹ HNO₃, wherein one resin disc was immersed and left under stirring for 24 h. Since acid dissolved agarose in most cases, leaving suspended Amberlite IRA-410 fragments in the solution, next to the elution procedure, all the eluates were filtered through cellulose acetate syringe filter after removing all the larger fragments of the discs.

2.6. General procedures for laboratory deployments

For all the following tests, before deployments, solutions remained in a controlled temperature oven (23 °C) with piston cap and support devices for 24 h. This procedure was adopted to ensure that the temperature of solutions was stabilized and any possible adsorption of the analyte in the containers would occur before immersion. Furthermore, in the case of pH influence test, this period was important to guarantee that changes in pH would not occur during immersion. After stabilization, the material was removed from the solution, and the devices were washed with ultrapure water and assembled as above described. The devices were deployed in duplicate for each time of the immersion curves and in triplicate for the other tests.

After predetermined periods, the devices were removed and immediately disassembled. The binding discs were transferred to 15 mL polypropylene tubes for elution.

The concentrations of the eluted solutions (and aliquots of deployment solutions) were analyzed by ICP OES for all in lab tests (immersion curve, pH, ionic strength and potential interfering ions) because of the sufficiently high concentrations of deployment solutions (20 ng mL⁻¹). Due to the necessity of lower detection limits, ICP-MS was employed for real samples and *in situ* performance tests.

Except when otherwise stated, the pH (adjusted by adding NaOH solution) and the ionic strength (adjusted with NaNO₃) of solutions were 0.03 mol L⁻¹ and 5.6, respectively. Temperature (23.5 ± 0.5 °C) was kept constant for all the tests.

2.7. Diffusion coefficient (immersion curves)

The determination of the diffusion coefficient of V(V) in agarose diffusive layer was calculated by rearranging Eq. (1) as follow:

$$D = (\alpha \Delta g) (C_b A)^{-1} \quad (4)$$

where α is the slope of the curve plotted with accumulated mass versus deployment time (ng s⁻¹).

The accumulation rate of V(V) by IRA-410-DGT (accumulated mass) was determined by deploying devices in solutions of known concentrations. Two tests were performed, the first one up to 46 h (A) (50 ng mL⁻¹ V, I = 0.03 mol L⁻¹ and pH = 5.4 ± 0.1) and the other one up to 72 h (B) (10 ng mL⁻¹ V, I = 0.03 mol L⁻¹ and pH = 5.4 ± 0.1). The devices were removed from solution after 4, 8, 12, 24 and 46 h for A and after 12, 24, 36, 48 and 72 h for B.

2.8. DGT method detection limits

The limit of detection (LOD) of the direct measurement by ICP-MS was determined, according to IUPAC recommendation [24], (n = 10).

The limit of detection for DGT technique (LOD_{DGT}) was calculated as the ratio of the instrumental LOD and the pre-concentration factor [25]. Pre-concentration factor was obtained by the ratio between the eluate concentration and the concentrations of the deployment solution (obtained by the direct measurement of aliquots of the deployment solution).

2.9. Effect of ionic strength and pH

To evaluate the effect of ionic strength on V(V) accumulation rate by IRA-410-DGT, four solutions containing 20 ng V(V) mL⁻¹ were prepared with pH adjusted to 5.5 and ionic strength adjusted with NaNO₃ solution to 0.0003, 0.003, 0.03, 0.3 and 1 mol L⁻¹, respectively. Then, three IRA-410-DGT devices were immersed in each solution for 6 h. Ionic strength was checked with the aid of a conductivity meter (Jenway) and the conductivity was converted to ionic strength according to the equation described elsewhere [26].

In a similar way, the influence of pH on V(V) accumulation rate by IRA-410-DGT was investigated by deploying the devices for 6 h in four solutions containing 20 ng V(V) mL⁻¹ (I = 0.03 mol L⁻¹) and pH values varying from 3 to 9.

2.10. Effect of potential interfering anions

To evaluate possible PO₄³⁻ and SO₄²⁻ interference on V(V) accumulation rate by IRA-410-DGT, four 20 ng V(V) mL⁻¹ solutions were prepared in the ratios of 1:250 (5 mg L⁻¹ PO₄³⁻, SO₄²⁻) and 1:1150 (23 mg L⁻¹ PO₄³⁻, SO₄²⁻), V:interfering ion, for both anions. Three IRA-410-DGT devices were deployed for 6 h in each solution (I = 0.03 mol L⁻¹, pH = 5.7 ± 0.2).

To evaluate the interfering effect of Cl⁻ (on Amberlite IRA-410 V accumulation rate and on V measurement by ICP-MS), three solutions containing 2 ng V(V) mL⁻¹ were prepared and NaCl were added to reach V:Cl⁻ ratios of 1:5000 (10 µg mL⁻¹ Cl⁻), 1:50,000 (100 µg mL⁻¹ Cl⁻) and 1:500,000 (1000 µg mL⁻¹ Cl⁻), respectively. Then, three DGT devices were deployed in each solution for 24 h (I = 0.03 mol L⁻¹, pH = 5.6 ± 0.1).

2.11. Comparison of V(V) accumulation rate by IRA-410-DGT and ferrihydrite binding agent in synthetic solutions

The accumulation rate of V(V) by IRA-410-DGT was evaluated in synthetic V(V) solutions with 10, 15 and 30 ng V mL⁻¹ (I = 0.03 mol L⁻¹, pH = 5.1 ± 0.1). For each solution, six DGT devices were immersed, three of those assembled as above described for IRA-410-DGT, and in the other three, the binding layer was replaced by ferrihydrite, prepared as previously described [27].

2.12. The mass accumulation rate of V(V) in natural samples (laboratory tests)

The performance of the proposed IRA-410-DGT devices was evaluated by deploying them in triplicate for 24 h in two samples. Sample A is a natural freshwater collected in a surrounding area of an Oil refinery. Sample B was collected from an acid drainage area, consequently an acid pH was found (pH = 3.3) for the sample. Sample B was spiked with 2 ng V(V) mL⁻¹ for recovery tests. The sample conditions of pH, ionic strength and temperature were respectively 7.0, 0.005 mol L⁻¹ and 22.5 ± 0.5 °C for Sample A and 3.3, 0.021 mol L⁻¹ and 22.9 ± 1.5 °C for Sample B.

2.13. In situ performance

Immersion of devices in the Piracicaba River for evaluation of *in situ* performance of the proposed method was carried out under

the coordinates 22° S 41' 44" W 47° 40' 19". Upstream of the sampling point, lies the Atibaia River, located in a densely populated area that includes in its territory a petrochemical complex. The uses of water for the region include public and industrial supply, domestic and industrial wastewater receiving, and irrigation [28].

Three IRA-410-DGT devices were immersed in the Piracicaba River for one week. Temperature, ionic strength and pH were measured (Table 1). Before the deployment and after the devices retrieval, two aliquots were collected and preserved in 2% HNO₃, one for measuring the total V concentration and another for measuring dissolved V concentration.

3. Results and discussion

3.1. Elution factor and diffusion coefficient

Table 2 shows data obtained from solid phase extraction (SPE) experiment using Amberlite IRA-410 discs as sorbent. The average elution factor calculated was 0.93 ± 0.08 , evincing that the adopted elution procedure was effective (quantitative and reproducible) for a wide range of concentrations. It was obtained an exchange capacity (in presence of NO₃⁻) of at least 27.0 μg V g resin⁻¹ and 40.8 μg V g resin⁻¹ for solution of 50 ng mL⁻¹ and 100 ng mL⁻¹, respectively. The obtained exchange capacity was achieved for the time frame of 6 h. Thus, for a longer period, the exchange capacity could be higher.

For the range wherein the V(V) accumulated mass by DGT versus deployment time was characterized by a linear behavior, the capacity of Amberlite-IRA-410 gels has not been exceeded and DGT works quantitatively. Figs. 1 and 2 show the linear range of deployment curves from tests A and B (item 2.6). For test A, the linear range achieved up to 24 h ($\alpha = 0.011$ ng s⁻¹ and $R^2 = 0.9993$). By using Eq. (4), the diffusion coefficient (D) obtained was $6.68 \pm 0.1 \cdot 10^{-6}$ cm² s⁻¹. For test B, the linear range was extended to 36 h ($\alpha = 0.0023$ ng s⁻¹ and $R^2 = 0.9834$). D value obtained was $7.58 \pm 0.5 \cdot 10^{-6}$ cm² s⁻¹. After these periods, the rate of V(V) accumulation was significantly decreased in both tests.

Therefore, an average D value of $7.13 \pm 0.6 \cdot 10^{-6}$ cm² s⁻¹ was adopted for following experiments. This value is similar to previously reported results values for polyacrylamide hydrogel, as shown in Table 3. A diffusion coefficient of $6.66 \pm 0.67 \cdot 10^{-6}$ cm² s⁻¹ in polyacrylamide gel was calculated from the average of values obtained throughout a pH range [13]. A similar value of $6.5 \pm 0.3 \cdot 10^{-6}$ cm² s⁻¹ was also reported for V(V) in polyacrylamide gel [14]. Also, values of $7.14 \pm 0.04 \cdot 10^{-6}$ cm² s⁻¹ and $8.02 \pm 0.35 \cdot 10^{-6}$ cm² s⁻¹ were reported by Panther et al [15] using DGT deployment curves and diffusion cell, respectively. Price et al. [17] obtained a D of $6.70 \pm 0.06 \cdot 10^{-6}$ cm² s⁻¹ in synthetic freshwater by diffusion cell and $6.73 \pm 0.08 \cdot 10^{-6}$ cm² s⁻¹ by DGT.

Recently, a value for the D of V(V) on agarose diffusive gel of

Table 1
Characterization of the Piracicaba River, São Paulo, Brazil.

pH	7.5
I, mol L ⁻¹	0.004
Temperature (n = 2), °C	22.5 ± 0.6
Total organic carbon	7.13 ± 0.16
Ions, mg L ⁻¹	
F ⁻	0.29
Cl ⁻	47
NO ₂ ⁻	0.40
NO ₃ ⁻	30
SO ₄ ²⁻	56
PO ₄ ³⁻	0.94

Table 2

Accumulation rate of V(V) by Amberlite IRA-410 discs obtained by solid phase extraction. M_r = retained mass average (n = 2); M_e = eluted mass average (n = 2); F_E = Elution factor. *Average elution factor.

Concentration, ng mL ⁻¹	M _r , ng	M _e , ng	F _E
5	148 ± 24	130 ± 17	0.88 ± 0.21
20	535 ± 61	480 ± 6	0.90 ± 0.12
50	1023 ± 66	1029 ± 116	1.01 ± 0.13
100	1604 ± 121	1460 ± 19	0.91 ± 0.08
			0.93 ± 0.08*

$8.64 \pm 0.21 \cdot 10^{-6}$ cm² s⁻¹ has been pioneering reported [23]. This value is 21 ± 8% higher than the one reported in this work.

The linearity of V(V) accumulation rate occurred up to 24 h for the deployment in 50 ng mL⁻¹ solution (Fig. 2), with 885 ± 35 ng accumulated by each IRA-410 disc. This value is not significantly different from the expected one when considering the results obtained by SPE (Table 2), wherein 967 ± 129 ng of V(V) were accumulated in the 50 ng mL⁻¹ solution. When considering the deployment in the 10 ng mL⁻¹ solution (Fig. 2), the maximum accumulation of 267 ± 7 ng of V(V) suggests that there is a decrease on V(V) accumulation rate with the decrease of the ratio V: NO₃⁻, likely due to competition of binding sites of the resin with NO₃⁻. Therefore, the decrease on V(V) accumulation rate after 24 h (50 ng mL⁻¹ solution) is likely to have occurred due to saturation of the binding sites of the resin, but for the 10 ng mL⁻¹ solution an earlier decrease on the accumulation rate of V(V) may be due to competition with other anions, such as NO₃⁻.

For comparison, Luo et al. [14] reported a linear range for V(V) when using slurry ferrihydrite up to 10 h (exchange capacity of approximately 20 μg disc⁻¹) and 20 h (exchange capacity of approximately 60 μg disc⁻¹) when using precipitated ferrihydrite. After these periods, the exchange capacity of the binding phase is likely to be reached, according to the authors.

3.2. DGT method detection limit

An instrumental limit of detection of 620 ng L⁻¹ was obtained using ICP-MS in normal mode operation. Considering a pre-concentration factor of 19 (24 h of deployment time) or 125 (168 h deployment time), LODs of 32 ng L⁻¹ and 4 ng L⁻¹ can be

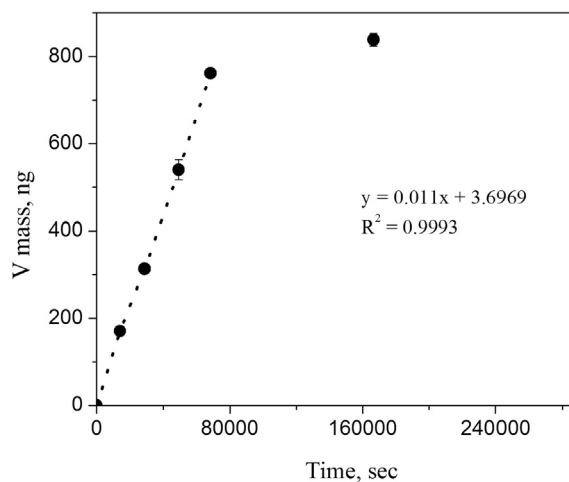


Fig. 1. V(V) retained mass (ng) versus time for test A. Linear range up to 24 h (50 ng V mL⁻¹; I = 0.03 mol L⁻¹ NaNO₃, pH = 5.5 and T = 23.5 ± 0.5 °C). Dashed line indicates the best fit of the data.

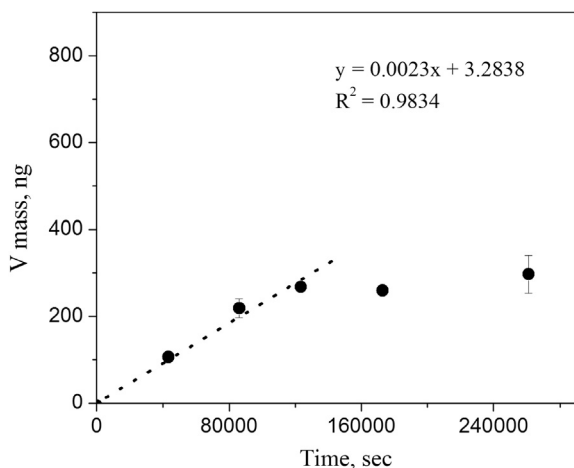


Fig. 2. V(V) retained mass (ng) versus time for test B. Linear range up to 36 h (10 ng V mL⁻¹; I = 0.03 mol L⁻¹ NaNO₃, pH = 5.5 and T = 23.5 ± 0.5 °C).

Table 3

Comparison of the obtained D and previously reported values.

	D (10 ⁻⁶ cm ² s ⁻¹)
This work	7.13 ± 0.3
Luo et al., 2010	6.5 ± 0.3
Österlund et al., 2010	6.72 ± 0.27
Price et al., 2013	6.73 ± 0.08
Panther et al., 2013	7.14 ± 0.04
Wang et al., 2016	8.64 ± 0.21

obtained with the proposed approach. These obtained values are significantly lower than mean values reported for superficial freshwater, wherein V concentration ranges from ranges 1–30 ng mL⁻¹ [2]. DGT method detection limit of previously reported approaches range from 7 to 280 ng L⁻¹ [13–15,17].

3.3. Influence of ionic strength

The results presented in Fig. 3 show the recoveries of V(V) as a function of ionic strength in the range from 0.0003 mol L⁻¹ to 1 mol L⁻¹ NaNO₃. For the range from 0.0003 mol L⁻¹ to 0.03 mol L⁻¹, V(V) concentration in each solution obtained by IRA-410-DGT devices (C_{DGT}) shows little variation compared to the values obtained by direct measurement of the aliquots (C_s), suggesting that the ionic strength did not affect the V(V) accumulation rate for this range. Lower V(V) accumulation rate can be observed for solutions with ionic strength greater than or equal to 0.3 mol L⁻¹ NaNO₃ (Fig. 3), which we attribute to the mass effect of NO₃⁻, more expressive in these solutions due to higher concentration of NaNO₃. Very similar ionic strength working range was reported by Whang et al. [16]. Other than that, the efficient recovery of V(V) in low ionic strength values stands out because it was either not observed, as Luo et al. [14] obtained a 20% reduction in the accumulation rate of the V(V) by ferrihydrite for ionic strength values lower than 0.0001 mol L⁻¹, or it was not previously reported [15].

3.4. Influence of pH

Fig. 4 shows the influence of pH on V(V) accumulation rate for the studied range. The ratio between C_{DGT} and C_s remained close to one, evincing a satisfactory performance of the technique for the whole pH range studied, although a lower accumulation rate was

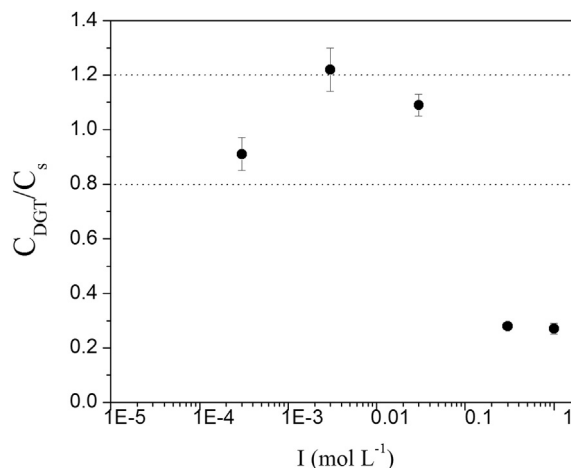


Fig. 3. Effect of the ionic strength on V(V) accumulation rate by Amberlite IRA-410 binding gel disc. Deployment time: 6 h (20 ng V mL⁻¹, pH = 5.5 and T = 23.5 ± 0.5 °C).

expected for the pH 3. For pH value of approximately 3, Luo et al. [14] reported a decrease of 40% on the V(V) accumulation rate by precipitated ferrihydrite, which was attributed to the greater presence of the cationic V(V) form (VO₂⁺) for lower pH conditions. Panther et al. [15] also observed an underestimation of the analyte concentration for pH values lower than 4, probably due its lower affinity to VO₂⁺, similarly as reported by Luo et al. [14]. For the pH range from 4 to 10 and from 4.42 to 8.45, Österlund et al. [13] and Whang et al. [16], respectively, reported that the method was independent of pH.

As V(V) accumulation rate was independent of pH for all the studied range, this approach provides the possibility of sampling under pH 4. Hence, the present method can be a tool in AMD areas sampling.

3.5. Interfering ions effect

Table 4 shows V(V) accumulation rate by IRA-410-DGT in the presence of PO₄³⁻ and SO₄²⁻. For solutions where the anions ratio was 1: 250, the V(V) recoveries obtained for SO₄²⁻ and PO₄³⁻ solutions were 98% and 92%, respectively. Increasing the ratio to 1: 1000, the recoveries obtained for SO₄²⁻ and PO₄³⁻ were 83% and 90%, respectively. Therefore, the obtained results evince the proposed

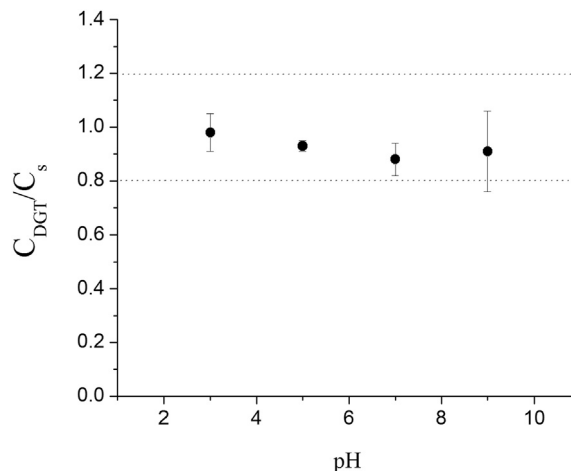


Fig. 4. Effect of pH on V(V) accumulation rate by Amberlite IRA-410 binding gel disc. Deployment time: 6 h (20 ng V mL⁻¹, 0.03 mol L⁻¹ NaNO₃ and T = 23.5 ± 0.5 °C).

Table 4
Effect of interfering ions on accumulation rate of V(V) by Amberlite - IRA 410. C_s = bulk solution concentration (n = 2); C_{DGT} = solution concentration given by DGT (n = 3).

		C_s , ng mL ⁻¹	C_{DGT} , ng mL ⁻¹	C_{DGT}/C_s
PO ₄ ³⁻	1:250	20.60 ± 1.57	18.94 ± 1.77	0.92 ± 0.12
	1:1000	19.90 ± 0.79	17.81 ± 1.27	0.90 ± 0.08
SO ₄ ²⁻	1:250	21.02 ± 1.24	20.65 ± 0.46	0.98 ± 0.06
	1:1000	21.36 ± 2.24	17.75 ± 0.57	0.83 ± 0.11

Table 5
- Effect of Cl⁻ interference on the determination of V by ICP-MS. C_E = expected concentration for the solution (n = 3); C_{DGT} = solution concentration given by DGT (n = 3); C_{ICP-MS} = bulk solution concentration given by direct measurement by ICP-MS (n = 2).

V:Cl	C_E , ng mL ⁻¹	C_{DGT} , ng mL ⁻¹	C_{ICP-MS} , ng mL ⁻¹	Without DGT	DGT
				C_{ICP-MS}/C_E	C_{DGT}/C_E
1:5000	1.9 ± 0.1	1.7 ± 0.1	2.08 ± 0.03	1.1 ± 0.1	0.9 ± 0.1
1:50,000	1.9 ± 0.1	1.8 ± 0.2	2.3 ± 0.1	1.2 ± 0.1	1.0 ± 0.1
1:500,000	1.9 ± 0.1	2.5 ± 0.2	4.1 ± 0.3	2.2 ± 0.1	1.3 ± 0.1

method potential for being efficiently applied to natural freshwaters, because the accumulation rate of V(V) in presence of SO₄²⁻ and PO₄³⁻ was satisfactory for the studied concentration range, which was similar to these ions concentration in rivers [29–31].

Except for Luo et al. [14], which considered the effect of NO₃⁻ in V accumulation rate by ferrihydrite, no other study has reported influence of specific interfering anions, as synthetic freshwater and seawater samples do evaluate the combined effect of interfering anions.

From Table 5 it can be observed the occurrence of an interference of 20% in ICP-MS direct measurement when V(V) is present in solution in a ratio V:Cl⁻ of 1:100,000, which is totally overcome when the determination is associated to DGT. For the solution where the ratio V:Cl⁻ is increased to 1:1000,000, an interference of more than 120% can be observed in the direct measurement. However it is minimized to only 33% when associated with DGT. No occurrence of interference was observed for the ratio 1:10,000.

Although interferences from Cl⁻ on V determination by Q-ICP-MS is possible, it was not studied in the papers wherein the V determination was carried out by Q-ICP-MS [14,15]. Price et al. [17] recommend the use of octapole collision/reaction cell to overcome spectral interferences on Q-ICP-MS measurements of other analytes.

Spectral interferences, as presented herein, can be minimized when the device is used in collision cell mode, as previously proposed by Bednar et al. [32]. However, the determination by these operating conditions reduces the sensitivity of the analysis for V, which, for ions found at very low concentrations (sub ng mL⁻¹), is not convenient.

The possibility of determining V(V) in waters with higher Cl⁻ concentrations is highly advantageous since both ions have increasing concentration reported in industrialized areas. Higher Cl⁻ concentrations have been reported for river waters subjected to

the runoff from roads deicing [33], industrial wastewater, oil well wastewater, agriculture runoff and mining activities, being reported an Cl⁻ level increase around 250 mg L⁻¹ [34]. Therefore, since Amberlite IRA-410-DGT overcame Cl⁻ interference within this range, V(V) concentration in rivers can be pursued by the use of the proposed method.

3.6. Performance on synthetic waters

Table 6 shows V(V) accumulation rate on Amberlite IRA-410 and ferrihydrite in concentrations ranging from 10 to 30 ng mL⁻¹. It can be observed that the ratio C_{DGT}/C_s obtained by Amberlite IRA-410-DGT were near to one (recoveries between 96 and 110%) and reasonably agreed with the values obtained by ferrihydrite, binding phase already assessed for V. Although, values were similar for both binding agents, in some situations, they were overestimated when using ferrihydrite. This overestimation is likely to be due to differences regarding F_E and diffusion coefficient from literature, which were used for the calculations, and the conditions wherein the present work was carried out.

3.7. Performance on natural freshwaters (laboratory tests)

Table 7 shows V(V) recovery in two real water samples with different characteristics. The values obtained by the propose approach agrees with the value obtained from the direct determination, showing recoveries between 93% and 109%. It should be noted that sample B is characterized by having pH = 3.3, as described in item 2.12. Notwithstanding, the obtained recovery by IRA-410-DGT for this sample was 109%, corroborating the results of pH influence test. Additionally, efficient recovery of sample B occurred in a matrix containing important potential interfering ion

Table 6
V(V) recovery by Amberlite IRA-410-DGT and ferrihydrite-DGT in synthetic waters. C_s = bulk solution concentration (n = 2); C_{DGT} = solution concentration given by DGT (n = 2).

Concentration, ng mL ⁻¹		Amberlite IRA-410	Ferrihydrite
10	C_s	10.02 ± 0.32	
	C_{DGT}	9.58 ± 1.31	12.94 ± 2.02
	C_{DGT}/C_s	0.96 ± 0.14	1.29 ± 0.16
15	C_s	15.67 ± 0.68	
	C_{DGT}	17.25 ± 2.59	20.61 ± 1.99
	C_{DGT}/C_s	1.10 ± 0.16	1.32 ± 0.11
30	C_s	29.51 ± 1.49	
	C_{DGT}	28.86 ± 0.20	35.78 ± 1.85
	C_{DGT}/C_s	0.98 ± 0.05	1.21 ± 0.07

Table 7

V(V) recovery by Amberlite IRA-410-DGT in natural waters. C_s = dissolved solution concentration ($n = 2$); C_{DGT} = solution concentration given by DGT (Sample A: $n = 2$; Sample B = $n = 3$).

	C_s , ng mL ⁻¹	C_{DGT} , ng mL ⁻¹	C_{DGT}/C_s
Sample A	1.92 ± 0.12	1.80 ± 0.07	0.93 ± 0.10
Sample B	0.80 ± 0.01	0.87 ± 0.01	1.09 ± 0.01

Table 8

In situ Amberlite IRA-410-DGT performance for the accumulation rate of V.

Total V ($n = 2$), ng mL ⁻¹	2.98 ± 0.01
Dissolved V ($n = 2$), ng mL ⁻¹	1.74 ± 0.03
C_{DGT} ($n = 3$), ng mL ⁻¹	1.66 ± 0.10
$C_{DGT}/\text{Dissolved V}$, %	95 ± 6

previously evaluated in this work, as 0.39 mg Cl⁻ L⁻¹, 2.13 mg NO₃⁻ L⁻¹ and 1052 mg SO₄²⁻ L⁻¹. Therefore, IRA-410-DGT allows the determination of V(V) concentration in samples which have pH lower than 4. Then, sampling V(V) in acid mining drainage becomes possible when its pH is higher than 3, which may be of great interest since V has been reported in mine tailings [35,36] and is present in carnotite, one important uranium ore [37] and coal [38].

3.8. *In situ* performance

Table 8 shows values obtained by the developed method and the direct measurement for immersion performed in the Piracicaba River, PCJ Basin, Brazil. A V(V) recovery by IRA-410-DGT of more than 95% of the dissolved V by direct determination was obtained. As it can be seen in Table 1, the concentration of Cl⁻ in the sample is within the range wherein DGT-IRA-410 is able to overcome the interference of Cl⁻ (1: 30,000, V: Cl) and it is not affected by the presence of PO₄³⁻ (1: 500). The concentration of SO₄²⁻ is higher than the margin found to the technique (1: 30,000, V: SO₄²⁻). However, the high content of this ion apparently showed no significant interfering effect, given the high recovery of the dissolved content. As the deployment in water samples considers interfering ions effect in its whole complexity, SO₄²⁻ is not likely to affect V sampling in freshwaters.

4. Conclusions

A new DGT method for V(V) determination based on the use of ICP-MS and the resin Amberlite IRA-410 is proposed. The obtained results show that the proposed method can be used for the determination of V(V) in natural freshwater. The accumulation rate of V(V) was linear up to at least 36 h. Also, V(V) accumulation rate was independent of pH for all the studied range which includes the possibility of sampling under pH 4, thus it provides the possibility to sample V(V) in AMD areas. It was satisfactory for ionic strength values from 0.0003 mol L⁻¹ to 0.03 mol L⁻¹, which allows its use in freshwaters of a wide variety of conditions. In some situations IRA-410-DGT provides a significant reduction of ³⁵Cl¹⁶O interference in V(V) determination by ICP-MS, assuring a sufficiently low LOD to permit V(V) determination without the use of approaches such as collision cell mode.

Laboratory tests performed in both natural and synthetic freshwater showed quantitative recoveries. The accumulation rate of V(V) through *in situ* deployment was also efficient corresponding to 95.5% of V dissolved concentration. Therefore, Amberlite IRA-410 is an effective binding layer to sample V(V) in DGT technique and which complements other available DGT methods for V(V)

sampling in waters. When compared with other binding materials used in DGT, Amberlite IRA-410 resin allowed measurements at lower pH and minimized Cl⁻ interference on V determination when DGT is associated with determination by quadrupole ICP-MS, because minimal amount of Cl⁻ is sampled avoiding formation of the polyatomic ion ³⁵Cl¹⁶O⁺.

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