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Speciation and preconcentration of vanadium(v) and vanadium(iv) in water samples by flow injection-inductively coupled plasma optical emission spectrometry and ultrasonic nebulization

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An on-line separation, preconcentration and determination system for vanadium(iv) and vanadium(v) comprising inductively coupled plasma optical emission spectrometry (ICP-OES) coupled to a flow injection (FI) method with an ultrasonic nebulization (USN) system was studied. The vanadium species were retained on an Amberlite XAD-7 resin as a vanadium–2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (V–5-Br-PADAP) complex at pH 3.7. Enhanced selectivity was obtained with the combined use of the formation on-line of the complexes and 1,2-cyclohexanediaminetetraacetic acid (CDTA) as masking agent. The vanadium complexes were removed from the microcolumn with 25% v/v nitric acid. A sensitivity enhancement factor of 225 was obtained with respect to ICP-OES using pneumatic nebulization (15-fold for USN and 15-fold for the microcolumn). The detection limit for the preconcentration of 10 mL of aqueous solution was 19 ng L^{-1}. The precision for 10 replicate determinations at the 5 μg L^{-1} V level was 2.3% relative standard deviation (RSD), calculated from the peak heights obtained. The calibration graph using the separation and preconcentration system for vanadium species was linear with a correlation coefficient of 0.9992 at levels from near the detection limits up to at least 100 μg L^{-1}. The method was successfully applied to the speciation of vanadium in river water samples.

Introduction

The chemical and physical properties of a metal species depend very much on its oxidation state, hence an accurate determination of each species is important for evaluating both the potential risk and benefits of some metals.[1,2] Vanadium has various oxidation states and ionic forms in aqueous solution. It exists in two different oxidation states, V(v) and V(iv), in well aerated natural and industrial waters.[3,4] The significance of vanadium speciation is that the two oxidation states have different nutritional and toxic properties.[5,6] The toxicity of V is dependent on its oxidation state, with V(v) being more toxic than V(iv).[3] Otherwise, the insulin-like properties of V, especially its effects on mitogenesis, suggest that the element plays a role in growth and development.[5] Therefore, the speciation and determination of V are receiving increasing attention in pollution and nutritional studies.

Since one of the routes of incorporation of V into the human body is water,[6–8] its determination in this type of sample is very important. The concentration of V in natural water is very low,[9–11] of the order of a few μg L^{-1}, hence powerful techniques are required and only a few of them show sufficient sensitivity. Neutron activation analysis (NAA)[12,13] has been applied to the determination of V, but it is time consuming and the routine analysis of numerous samples is laborious. This method also requires sophisticated instrumentation which may not be available in most analytical laboratories. Inductively coupled plasma mass spectrometry (ICP-MS)[14,15] is used for the determination of V because of its high sensitivity, high selectivity and high sample throughput. However, the cost of the instrumentation may be prohibitive to many laboratories.

Inductively coupled plasma optical emission spectrometry (ICP-OES) or electrothermal atomic absorption spectrometry (ETAAS) are the most commonly used techniques for the determination of traces of V, but the low level of V concentration in water is not compatible with the detection limits of these techniques. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of the analyte elements in the sample are too low to be determined directly by ICP-OES.

Many separation and preconcentration techniques[6,16,17] for the determination of V(v) and V(iv) species have been proposed, including chelation and extraction, precipitation and the use of ion-exchange resins. However, many of these methodologies are performed in batch, thus requiring large sample volumes in order to reach low detection limits. Further, these systems have higher contamination risks and are not practical for application in routine analysis. This situation has been significantly improved by utilizing flow injection (FI) associated with ICP-OES.[18,19] In fact, to date the most dramatic improvements achieved in FI-ICP-OES have been in the field of on-line preconcentration.[20,21] On the other hand, the use of an ultrasonic nebulizer can provide a 5–50-fold improvement in detection limits.[22–24]

XAD resins have been used as packing materials in preconcentration columns for FI.[25,26] They have been employed as supports for the immobilisation of chelating agents and metal complexes.[27–29] 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) forms stable complexes with numerous metal ions,[30,31] and is therefore a suitable reagent for V preconcentration on an XAD resin.[32] Recently we have reported a preconcentration FI system for the determination of total V

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using 5-Br-PADAP.[33] However, in that work, the complexes were formed in batch, prior to retention on the resin, and this only allowed the preconcentration and determination of total V and the speciation of V(IV) and V(V) was not possible. On the other hand, selectivity in metal complexing with organic reagents can be enhanced by the use of masking agents.[34]

In this work, a fully on-line method is proposed for complexing, separation and preconcentration of V(V) and V(IV) using an XAD-7 resin. Vanadium was retained on the resin in the form of a V–(5-Br-PADAP) complex. Determination selectivity was enhanced by the use of 1,2-cyclohexanediaminetetraacetic acid (CDTA) as masking agent for V(IV). The determination was performed using ICP-OES associated with FI methodology and an ultrasonic nebulization (USN) system.

Experimental

Instrumentation

The measurements were performed with an ICP 2070 sequential ICP spectrometer (Baird, Bedford, MA, USA). The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. A U-5000 AT ultrasonic nebulizer (CETAC Technologies, Omaha, NE, USA), involving a desolvation system, was used. The ICP operating conditions were identical with those reported previously.[33] The ultrasonic nebulization conditions were heater temperature 140 °C, condenser temperature 4 °C and carrier gas flow rate 1.0 L min^{-1}. The FI system used is shown in Fig. 1. A Minipuls 3 peristaltic pump (Gilson, Villiers-le-Bel, France) was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 5041 four-way rotary valve. Two coiled reactors L_1 (0.65 m × 0.7 mm id) and L_2 (3.0 m × 0.7 mm id) were prepared using PTFE tubing. For sorption of the complex, a microbore glass column (50 mm × 3 mm id) fitted with porous 25 μm glass frits was used as the resin holder. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent. The 309.311 nm spectral line was used.

Reagents and chemicals

A 10^{-2} M solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

A 10^{-2} M solution of CDTA (Aldrich) was prepared by dissolution in 0.1 M sodium hydroxide (Aldrich) solution.

Vanadium(V) standard solution, 1000 μg mL^{-1}, was prepared by dissolving 2.2966 g of ammonium metavanadate (99.99%) (Merck, Darmstadt, Germany) in 1000 mL of ultrapure water.

Vanadium(IV) standard solution, 1000 μg mL^{-1}, was prepared by dissolving 4.9682 g of $VOSO_4 \cdot 5H_2O$ (99.99%) (Merck) in 1000 mL of ultrapure water containing 2 mL of concentrated sulfuric acid.

Acetic acid–acetate buffer solution was prepared from 2 M acetic acid solution adjusted to pH 3.7 by dissolution of sodium hydroxide.

Ultrapure water (18 MΩ cm^{-1}) was obtained from a EASYpure RF system (Barnstead, Dubuque, IA, USA).

Sample collection and preparation

River water samples were filtered through 0.45 μm pore size membrane filters (Millipore, Bedford, MA, USA) immediately after sampling, and were acidified to pH 2 with nitric acid and stored at 4 °C in Nalgene bottles (Nalge, Rochester, NY, USA). All the instruments used were previously washed with 10% v/v HNO_3 and then with ultrapure water.

Separation and preconcentration procedure

Before loading, the column was conditioned for preconcentration at the correct pH with buffer diluted solution (1 + 10), valve V_1 in position B (Fig. 1). For the determination of V(V) (valve V_1 in position S), 10 mL of aqueous sample solution containing V (at a flow rate of 5.0 mL min^{-1}) and 10^{-4} M CDTA (at a flow rate of 1.5 mL min^{-1}) were previously mixed on-line in the reactor (L_1), where V(IV) was masked. The resulting solution was combined on-line with 4×10^{-4} M 5-Br-PADAP in 35% v/v ethanol (at a flow rate of 1.5 mL min^{-1}), buffered to pH 3.7 with acetic acid–acetate, to form the metal complex. This mixture was pumped through the reactor (L_2) and V(V) was totally complexed by the reagent 5-Br-PADAP. The solution was then loaded on the XAD-7 resin at a flow rate of 8 mL min^{-1} with valve V_2 in load position (a). After the loading time, the sample still present in the lines and the column was removed by further washing with buffer diluted solution, with valve V_1 again in position B. Finally, valve V_2 was switched to the injection position (b) and the retained metal complex was

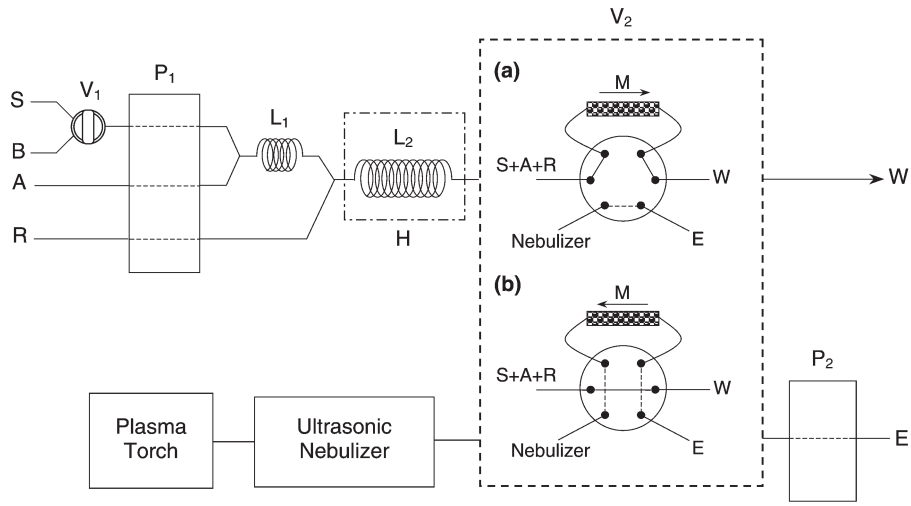

Fig. 1 Schematic diagram of the instrumental set-up. B, Buffer diluted; S, sample (flow rate 5.0 mL min^{-1}); R, 4×10^{-4} M 5-Br-PADAP solution (1.5 mL min^{-1}); A, ultrapure water or 10^{-4} M CDTA (flow rate 1.5 mL min^{-1}); L_1 and L_2, reactors; E, eluent (flow rate 1.5 mL min^{-1}); W, waste; P_1 and P_2, peristaltic pumps; H, water-bath; M, microcolumn; V_1, two-way valve; V_2, load–injection valve [(a) load position; (b) injection position].

eluted in countercurrent (*i.e.*, reversal of the flow direction through the column during elution with respect to sample loading) with 25% v/v HNO_3 at a flow rate of 1.5 mL min^{-1}, directly in the ultrasonic nebulizer and ICP-OES. For determination of total V, the above described procedure was followed, but with mixing of the sample with ultrapure water in the reactor (L_1) in order to reproduce the flow rates of V(v) preconcentration and determination. The mixture was then heated with 5-Br-PADAP reagent in the reactor (L_2) and placed in a water-bath (H) at a temperature of 60 °C. In this way, total complexation of V(v) and V(iv) was obtained. V(v) and V(iv) were subsequently loaded on the XAD-7 resin and finally eluted with 25% v/v HNO_3. The operating conditions were established and the determination was carried out. FI system measurements were expressed as peak-height emission, which was corrected against the reagent blank. The concentration of V(iv) was calculated by difference between the total concentration of V and that of V(v).

Results and discussion

Optimization of the loading and elution variables

The retention conditions of the metal complexes were optimised and the V signal was monitored by measuring it with ICP-OES while changing the pH of the solution that passed through the sorption micro-column. The optimum pH values were in the range 2.8–4.2. This phenomenon is understandable, since better complexation occurs within this range. Considering these results, the pH selected was 3.7. Working at this pH value had the advantage of selectively complexing and preconcentrating V, since most metal ions which can form complexes with 5-Br-PADAP do so at higher pH values.[30,31]

In the present work a bead size of resin of 20–50 mesh was considered adequate for the preconcentration procedure in the micro-column. Smaller resin particles could have improved the retention capacity, but this would have increased the back-pressure of the micro-column, and the flow rate ought to have been reduced, with a subsequent increase in preconcentration time. Our choice of the Amberlite XAD-7 resin was motivated by the fact that it is highly stable in both acidic and basic solution and exhibits an adequate surface area. This allows the use of the micro-column for an indefinite number of samples without degradation of performance, after using 25% v/v HNO_3 as eluent. Many researchers have studied the behaviour of Amberlite XAD resins as adsorbents of organic substances and as supports for chelating agent-impregnated resins.[26,32,35] Parrish[35] considered the greater water regain of Amberlite XAD-7 as the most important factor for a better exchange rate, independent of the surface area and pore diameter. Lee *et al.*[26] pointed out that in spite of having a lower distribution coefficient for XAD-7 than that obtained for XAD-4, XAD-7 can be swollen in aqueous solution and is better for use in a column.

It is well known that the retention of complexes on XAD resins is modified by the concentration of organic solvents.[32] Furthermore, the formation of metal complexes with 5-Br-PADAP is also affected by the solvent. Higher retention was observed for lower ethanol percentages. The value selected was 6.5% v/v, since it was the lowest value compatible with the stability of the complex.

As regards the variation of response with the molar ratio between 5-Br-PADAP reagent and V, the signal remained constant between 10 : 1 and at least 100 : 1.

The dimensions of the micro-column used here have been optimised and reported previously.[33,36] The sample flow rate through the microcolumn is a very important parameter, since this is one of the steps that controls the time of analysis. It could be verified that with a sample flow rate of 5 mL min^{-1} the analyte recovery was approximately 90%.

The elution conditions were optimized following the procedure described in a previous paper.[33] The optimum elution conditions of the V–5-Br-PADAP complex from the resin were identical with those found previously. Countercurrent elution (*i.e.*, reversal of the flow direction through the column during elution with respect to sample loading) substantially improved the elution profiles as compared with unidirectional flow.

On-line complexing of vanadium

In a previous paper,[33] we reported that no difference was obtained as regards V(v) and V(iv) complexation and retention on an XAD resin when the complexes were formed in batch before column loading. In the present work, we studied the effect of on-line complexing on the formation of the V(v) and V(iv) complexes with 5-Br-PADAP reagent. The complexes were formed on-line and retained on the resin, eluting in a final volume of 10 mL. Subsequently, measurement was performed by ICP-OES-USN. This procedure was performed for different reactor (L_2) lengths and working at room temperature. As can be seen in Fig. 2, a length of 3.0 m was sufficient to obtain total complexing of V(v).

Effect of temperature

The effect of temperature on the complexing reaction of V(iv) with 5-Br-PADAP reagent was studied by heating the coiled reactor L_2 in a water-bath. Preconcentration procedures for V(v) and V(iv) were developed and the signals obtained were evaluated at different bath temperatures. Once the on-line complexes had been formed, elution was performed to a final volume of 10 mL and measurement were carried out by ICP-OES-USN. In Fig. 3, it can be observed that an increase in the reaction temperature led to an increase in V(iv) complexation, which reached a maximum at 60 °C and remained constant at higher temperatures. Thus, working at 60 °C, total complexation of both oxidation states and subsequent retention on the resin were possible. Under these conditions, the retention was 90% for V(iv) and V(v). It can be also seen from Fig. 3 that temperature had no effect on the complexing of V(v) with 5-Br-PADAP.

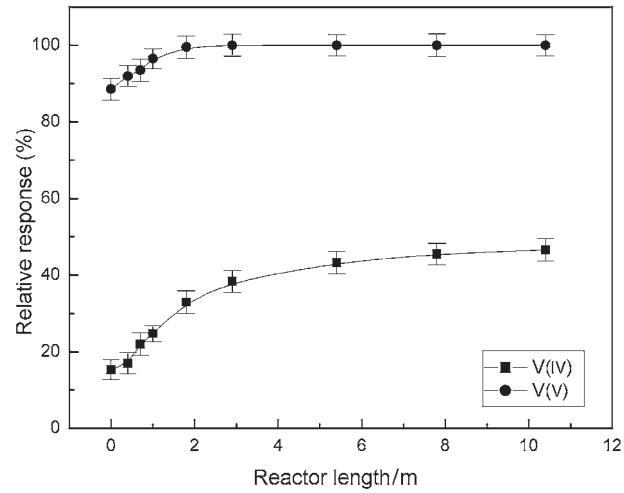

Fig. 2 Effect of the length of the L_2 reactor on the formation of the V–5-Br-PADAP complexes. Loading flow rate, 5 mL min^{-1}; V concentration, 50 μg L^{-1}; 5-Br-PADAP concentration, 4×10^{-4} M.

Masking reagent and selectivity

When on-line formation of the V complexes was performed at room temperature, differences in the complexing rates were observed between V(v) and V(iv), comparted with those observed in batch. This phenomenon appeared particularly useful considering the possibility of separation of the two oxidation states. However, even at room temperature, the V(iv)–5-Br-PADAP complex was only partially formed and retained on the resin. Therefore, with the purpose of obtaining the total separation of V(v) and V(iv), we studied the use of a masking agent. CDTA, which has been widely used as a masking agent in determinations of several metal ions that involve complex-forming reactions, was proposed here for masking V(iv) in the complexation with 5-Br-PADAP. Fig. 4 shows the masking effect of CDTA on V(iv), with a concentration of 2×10^{-5} M CDTA allowing for total masking of V(iv). The concentration selected for this work was 10^{-4} M CDTA. On the other hand, no retention of the V(iv)–CDTA complex on the XAD-7 resin was observed.

Interferences

Experiments were performed to discover the degree to which the proposed method is susceptible to interference from Al and Mg. The determination of V was possible in the presence of a great excess of Al and Mg since these elements were not complexed with 5-Br-PADAP under the operation conditions used. The effects of representative potential interferent species were tested. Thus, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+} could be tolerated up to at least 2500 μg L^{-1}. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the resin. This is explained by the fact that 5-Br-PADAP forms stable complexes with various elements (including Ca^{2+} and Mg^{2+}) at elevated pH. In fact, concentrations as high as 1000 mg L^{-1} for each of the compounds were easily tolerated. On the other hand, the amounts of anions usually present in river water samples (S^{2-}, CO_3^{2-}, F^-, SO_4^{2-}, Cl^-, PO_4^{3-}) do not produce any interference. The value of the reagent blank signal was not modified by the presence of the potentially interfering ions assayed.

Performance of the separation and preconcentration system

The overall time required for preconcentration of 10 mL of sample (2 min, at flow rate of 5 mL min^{-1}), washing (0.2 min), elution (0.45 min) and conditioning (0.25 min) was about 2.9 min. Hence the sample throughput was about 20 samples per hour. A sensitivity enhancement factor of 225 was obtained with respect to ICP-OES using pneumatic nebulization (15-fold for USN and 15-fold for the column).

Separation of vanadium(iv) and vanadium(v)

In order to assess the selectivity of the proposed method for V(iv) and V(v), it was applied to various synthetic samples and using different concentration relationships between the two oxidation states. In Table 1, it can be observed that the two species of V are completely separated and recovered quantitatively using the proposed method. The method was thus shown to have an acceptable accuracy under different conditions, with

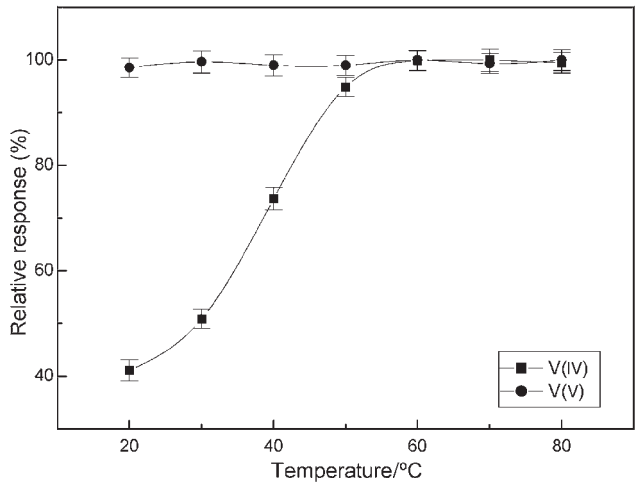

Fig. 3 Variation of V(iv) and V(v) complexation as a function of reaction temperature. Loading flow rate, 5 mL min^{-1}; V(v) concentration, 50 μg L^{-1}; 5-Br-PADAP concentration, 4×10^{-4} M; 25% v/v HNO_3 was used as eluent.

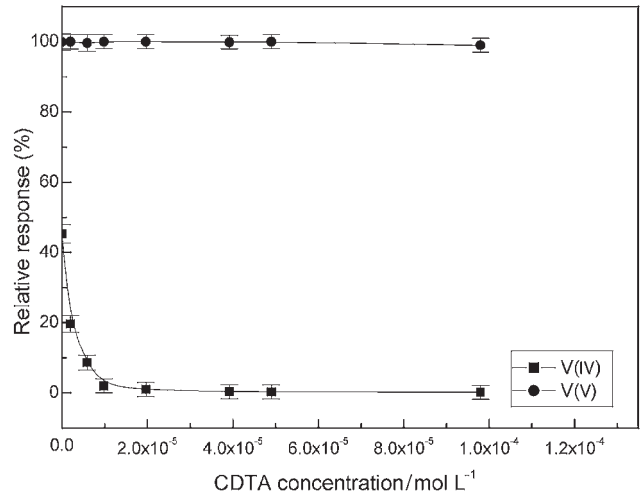

Fig. 4 Effect of the CDTA concentration on the separation of V(iv) and V(v). Loading flow rate, 5 mL min^{-1}; V concentration, 50 μg L^{-1}; 5-Br-PADAP concentration, 4×10^{-4} M.

Table 1 Evaluation of the separation of V(iv) and V(v) species

	Vanadium(iv)			Vanadium(v)		
V(v):V(iv) ratio	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)
0.025	100	101.20	101.2	2.5	2.45	98.0
0.125	40	40.0	100.0	5	4.93	98.7
0.5	20	19.90	99.5	10	9.90	99.0
2	10	9.92	99.2	20	20.50	102.5
8	5	4.87	97.3	40	39.92	99.8
40	2.5	2.46	98.4	100	100.30	100.3

Table 2 Concentrations of V(IV) and V(V) in river water samples (95% confidence interval; $n = 6$)

	Vanadium(IV)			Vanadium(V)		
Sample No.	Added/ μg L^{-1}	Found/μg L^{-1}	Recovery (%)[a]	Added/ μg L^{-1}	Found/μg L^{-1}	Recovery (%)[a]
1	0	0.84 ± 0.02	—	0	1.16 ± 0.02	—
	2	2.84 ± 0.02	100.0	2	3.15 ± 0.02	99.5
2	0	0.52 ± 0.03	—	0	0.76 ± 0.03	—
	2	2.48 ± 0.02	98.0	2	2.76 ± 0.03	100.0
3	0	1.21 ± 0.02	—	0	0.98 ± 0.02	—
	2	3.20 ± 0.02	99.5	2	2.94 ± 0.02	98.0
4	0	0.33 ± 0.02	—	0	0.58 ± 0.03	—
	2	2.74 ± 0.03	100.5	2	2.55 ± 0.02	98.5

[a] [(Found − base)/added] × 100.

recoveries varying between 97.3 and 101.2% for V(IV) and between 98.0 and 102.5% for V(V).

Determination of vanadium in water samples

Vanadium can be found in different oxidation states and forms (soluble, insoluble and organic complex forms) in natural waters. However, in sufficiently aerated waters, the most commonly found oxidation states are V(IV) and V(V). Hirayama *et al*.[6] determined that, in natural waters, the highest proportion of V corresponded to soluble forms, and Bosque-Sendra *et al*.[17] found that V exists mainly in soluble forms in river water. Taking this into account, the proposed method was applied to the determination of soluble V(IV) and V(V) in several river water samples.

The relative standard deviation (RSD) for 10 replicates containing 5 μg L^{-1} of V was 2.3%. The calibration graph was linear with a correlation coefficient of 0.9992 at levels from near the detection limit (DL) up to at least 100 μg L^{-1}. The DL, calculated as the amount of V required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ), was 19 ng L^{-1}. Finally, the results of the method applied to V(IV) and V(V) determination in water samples are shown in Table 2. The concentrations were in the range 0.33–1.21 μg L^{-1} for V(IV) and 0.58–1.16 μg L^{-1} for V(V). The results obtained are in good agreement with those of Hirayama *et al*[6] and Bosque-Sendra *et al*.[17] These authors found similar V(IV) and V(V) concentrations in river water samples.

Conclusions

The on-line formation of V–5-Br-PADAP complexes together with the use of CDTA as a masking agent and XAD-7 resin allowed the separation and determination of V(V) and V(IV). The on-line coupling of an FI sorption preconcentration system with ICP-OES increases the speed of the preconcentration and analysis process and reduces sample consumption and contamination risks. The proposed system of preconcentration associated with ultrasonic nebulization allows the separation and determination of the soluble forms of V(IV) and V(V) in natural water samples at levels as low as sub-μg L^{-1} with good accuracy and good reproducibility.

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