Selective Determination of V(IV) and V(V) in Seawater by Solid Phase Extraction and Electrothermal Atomic Absorption Spectrometry

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INTRODUCTION

Vanadium is usually present in the environment at low concentrations, but the levels can be increased in certain areas due to emission from different processes such as the metallurgical industry or the manufacture of corrosion-resistant alloys (1,2). The typical seawater concentration is in the 30–50 nM range (3), and the concentration in river water is around 15 nM (4). The dissolved vanadium concentrations reported for the Galician coast seawater samples are between 18–35 nM (5).

Vanadium (V) is considered an essential trace element at low concentration levels ($0.2\text{--}29.0\text{ }\mu\text{g L}^{-1}$ in water) and is beneficial for normal cell growth (6). However, at high concentrations (mg L^{-1} levels) it is toxic and results in carcinogenic effects and produces damage to liver and kidney (7). The toxicity of vanadium depends not only on its concentration but also on its chemical form. It can exist in fresh water and seawater as V(IV) and V(V), the latter being the most toxic form (8,9). Due to their toxicity properties, the determination of the concentration of each species is extremely important.

Fresh Water Sample Analysis

Several methods have been reported in the literature for vanadium speciation. Nakano et al. (10) reported the fractional determination of V(IV) and V(V) in fresh water using a catalytic method

ABSTRACT

A selective and sensitive method was developed for the separation and preconcentration of V(IV) and V(V) from seawater samples using a Chelex®-100 column. The influence of different parameters in the separation procedure such as pH of the sample, volume and concentration of extracting agents [NH_3 for V(V) and HNO_3 for V(IV)], sample load flow rate and the eluting flow rate were studied. The separated species were then determined by electrothermal atomic absorption spectrometry (ETAAS).

The limits of detection (LODs) and limits of quantification (LOQs) obtained using 50 mL of a seawater sample were 0.15 and $0.50\text{ }\mu\text{g L}^{-1}$, respectively, for V(IV) and 0.10 and $0.33\text{ }\mu\text{g L}^{-1}$, respectively, for V(V). The recovery percentages were $95.3 \pm 3\%$ and $92.3 \pm 3\%$ for V(IV) and V(V), respectively. The method was applied to the V(IV) and V(V) determination in seawater samples from the Galician coast. The only species detected in the three samples studied was V(V), which is the most toxic form and was found in concentration levels ranging from 0.1 to $0.25\text{ }\mu\text{g L}^{-1}$. The method is simple, quick, and low cost.

combined with the solvent extraction N-cinnamoyl-N-(2,3-xylyl) hydroxylamine (CXA). Okamura et al. (11) developed an automated method for the determination of vanadium (IV) and (V) in fresh water based on chelating resin separation and catalytic detection with Bindschedler's green leuco base. Chia-Ching Wann et al. (12) deter-

mined vanadium species in water samples by liquid chromatography coupled with plasma mass spectrometry and using a silica-based CRC_8 reversed-phase column. Soldi et al. (13) studied the mechanism of V(V) and V(IV) separation by sorption on an iminodiacetic chelating resin (Chelex®-100). These authors proposed the sorption of both species at a pH of approximately 4.5 and separating them by sequentially stripping V(V) at a pH of approximately 10 and then V(IV) at a pH of approximately 0.8. Based on this work, Deli Wang et al. (14) further developed an analytical protocol for the determination of V(IV) and V(V) in seawater samples. These authors used a solid-phase extraction of both species at pH 4.5 with Chelex-100, followed by the elution of V(V) with 0.1M ammonium hydroxide and the elution of V(IV) with 0.2N perchloric acid. The species eluted were dried on a hot plate and re-dissolved in 2 mL of 0.1N HNO_3 . The quantification of both vanadium species was performed by ETAAS. Amberlite XAD-7 (15) has also been used for the speciation and preconcentration of vanadium species from water samples by flow injection-inductively coupled plasma optical emission spectrometry (FI-ICP-OES). Vanadium was retained on the resin in the form of V-(5-Br-PADAP) complex, and 1,2-cyclohexanediamine-tetraacetic acid (CDTA) was used as masking agent for V(IV). The concentration of V(IV) was calculated by the difference between the total concentration of V and V(V). Hayati Filik et al. (16) reported a method for the simultaneous preconcentration of vanadium (V/IV) species with

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palmitoyl quinolin-8-ol bonded to Amberlite XAD-2 prior to simultaneous speciation analysis. The preconcentrated species were then quantitatively eluted from the resin column using HCl as the stripping agent. Total vanadium concentration was determined in the eluted fraction using 4-(2-pyridylazo)-resorcinol (PAR) by spectrophotometric detection at 542 nm. Vanadate was then quantified by masking vanadyl with 1,2 cyclohexanediamine-tetraacetic acid (CDTA).

Seawater Sample Analysis

In the method developed by Nukatsuka et al. (17), V(IV) was extracted from seawater samples as metal complexes with Chromazurol B (CAB) using the suspension of an anion-exchange resin. V(V) was extracted in the same way but using N-cinamoyl-N-2,3-xylyl-hydroxylamine (CXA) as the extracting agent. The species were then determined in the suspension by ETAAS. ZuLiang Chen et al. (18) developed an on-column complexation method for the simultaneous determination of V(IV) and V(V) in groundwater. The vanadium species were chelated with ammonium polycarboxylic acid to form anionic complexes, which were separated by capillary zone electrophoresis and determined using direct ultraviolet (UV) detection.

Proposed Method

In this work, a method for V(IV/V) separation and preconcentration using a Chelex-100 column and determination by ETAAS was developed. This method is based on the previous study developed by Soldi et al. (13) for V(IV/V) separation using a Chelex-100 column and eluting V(V) at basic pH (with ammonia) and V(IV) in an acid pH (with perchloric acid). The method was applied to the determination of these vanadium species in seawater samples from the Galician coast (Northwestern Spain).

EXPERIMENTAL

Instrumentation

Measurements were performed using a PerkinElmer® Model 1100B atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA), equipped with an HGA®-700 graphite furnace atomizer and an AS-40 autosampler. The source of radiation was a vanadium hollow cathode lamp (Cathodeon, Cambridge, UK). Pyrolytically coated graphite tubes with L'vov platforms were used for the analysis. For all measurements made during this study, integrated absorbance was used with an integration time of six seconds. The temperature and time programs for the atomizer and the instrumental parameters are listed in Table I. The sample volume injected was 20 µL.

A Rheodyne® Model 7060RV, 6 Position/6 Port standard valve (Bensheim, Germany) and a Model Minipuls™-3 peristaltic pump (Gilson, Villiers le Bel, France) were used in the vanadium separation and preconcentration step. The sample pH was measured with a Thermo Orion Model 720 pH meter (Thermo Orion, Beverly, MA, USA). Other instrumentation used during sample preparation included a Sartorius Model BP121S analytical balance (Sartorius, Goettingen, Germany), a polytetrafluoroethylene (PTFE) column (5 cm length,

3 mm i.d.), and polyethylene (PE) tubing and connectors from Gilson, France, S.A. and PerkinElmer, Inc..

Standard Solutions and Reagents

The stock standard solutions of 1000 mg L⁻¹ vanadium (V), (NH₄VO₃ in HNO₃ 0.5M), and vanadium (IV), (VOSO₄ in 8.6% H₂SO₄), were purchased from Merck (Darmstadt, Germany).

The buffer solution used was 0.1 mol L⁻¹ acetic acid-sodium acetate (HAc-NaAc) (Panreac, Barcelona, Spain).

NH₃ (25%) and HNO₃ (69%) were from Panreac.

Argon N50, 99.999% purity, was used as a sheath gas for the atomizer and to purge internally.

All dilutions were performed with Milli-Q® water (18 MΩ cm, Millipore Corporation, Bedford, MA, USA).

All glassware was kept in 10% nitric acid for at least 48 hours and washed three times with ultrapure water before use.

Sample Collection and Preparation

Seawater samples were collected from the Arousa Estuary (Northwestern Spain) using a Niskin bottle. The samples were filtered through 0.45-µm pure membrane

TABLE I
Graphite Furnace Conditions for V(IV) and V(V)
Determination by ETAAS

Step	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Ar Flow (mL min ⁻¹)
Dry	110	10	40	300
Pyrolysis	1500 ^a /1600 ^b	5	10 ^a /8 ^b	200
Atomization	2700	0	6	0 (read)
Cleaning	2750	1	5	300

^a V(IV) determination in HNO₃ media.

^b V(V) determination in NH₃ media.

Spectrometric parameters: lamp current, 40 mA; injection volume, 20 µL; wavelength (λ), 318.4 nm; slit width, 0.7 nm; background correction, D₂ lamp.

filters immediately after sampling and stored at 4 °C in polyethylene bottles prior to analysis.

Preparation of Chelating Resin

Chelex-100 chelating ion exchange resin (sodium form) (Sigma-Aldrich, Sydney, Australia), with a particle size range of 50–100 mesh, was introduced into a PTFE column. To avoid loss of particles when the sample solution passes through the column, a small amount of quartz wool was placed at both ends of the column. The column was then connected to a peristaltic pump with PerkinElmer tubing.

Iminodiacetic chelating resin was converted to the H^+ form using the procedure described previously by Pesavento et al. (19). First, the resin was washed with ultrapure water and converted to the hydrogen form using a column procedure by passing 10 bed volumes of 0.1 M

HCl. The column was then washed with ultrapure water and conditioned to pH 4.5 using 5 mL HAC: NaAc (0.1M) as a buffer solution.

On-line Preconcentration and Separation Procedure

Separation and preconcentration of the vanadium species from seawater samples was performed using a conditioned Chelex-100 column as described in the “Preparation of Chelating Resin” section. First, 50 mL of seawater sample or vanadium standard was loaded onto the column at a flow rate of 0.83 mL min^{-1} . In the second step, 5 mL of 0.1M HAC:NaAc buffer solution (pH=4.5) was passed through the column at 0.83 mL min^{-1} . Afterwards, V(V) was eluted with 5 mL of 0.1M NH_3 at 0.83 mL min^{-1} and, finally, 8 mL of 0.1M HNO_3 at 0.83 mL min^{-1} was passed through the column to elute the V(IV) species. The vanadium concentration was determined in both fractions by

ETAAS using the instrumental conditions listed in Table I. The flow injection system for preconcentration and separation of the vanadium species is shown in Figure 1.

RESULTS AND DISCUSSION

The separation and preconcentration of V(IV) and V(V) from seawater samples was developed using a Chelex®-100 column and NH_3 and HNO_3 as the eluting agents. The separated species were then determined by ETAAS. Therefore, the operating conditions for vanadium determination by ETAAS as well as the variables affecting the separation species were optimized.

Optimization of Graphite Furnace Program for Vanadium Determination by ETAAS

After the preconcentration step, the vanadium species on the Chelex-100 column were selectively eluted using NH_3 [for V(V)] or HNO_3 [for V(IV)] as the eluting agent. The graphite furnace program was optimized using a solution of 50 $\mu g L^{-1}$ V(V) in 0.1 M NH_3 and 50 $\mu g L^{-1}$ V(IV) in 0.1 M HNO_3 . The influence of the mineralization temperature on the integrated absorbance was studied in the range of 500–2500 °C for both species. The results obtained for this experiment are shown in Figure 2. The optimum mineralization temperatures were 1600 and 1700 °C for V(IV) and V(V), respectively.

Similarly, the atomization temperature was studied in the range of 1800–2700 °C (Figure 2). The latter temperature was selected as optimum for both species. Finally, the ramp and hold times for all steps of the graphite furnace program were optimized. The final graphite furnace conditions for V(IV) and V(V) determination by ETAAS are listed in Table I.

Fig. 1. Preconcentration and separation system.

Fig. 2. Influence of the mineralization and atomization temperatures in the integrated absorbance signal for V(IV) and V(V) determination by ETAAS.

Optimization of Separation Conditions

Experiments were designed for the optimization of the vanadium separation procedure. The influence of different variables such as pH, NH_3 , and HNO_3 concentration, NH_3 and HNO_3 volumes, sample load flow rate and elution flow rate were investigated.

The first parameter studied was the pH of the sample. The influence of the pH in the retention of both species in the column was studied using a synthetic seawater sample spiked with $21.9 \mu\text{g L}^{-1}$ of either V(IV) or V(V). The pHs were selected based on studies previously developed by Soldi et al. (13) for vanadium speciation in water samples. Therefore, 50 mL of a seawater sample spiked with either V(IV) or V(V), at a pH between 2 and 7 (adjusted with 0.1 M acetate buffer), was loaded onto the column at 10 rpm. Afterwards, the column was washed using 5 mL of 0.1M acetate buffer. Then, V(V) was eluted with 6 mL of 0.1M NH_3 at a flow rate of 0.83 mL min^{-1} ; V(IV) was eluted with 10 mL of 0.2M HNO_3 at the same flow rate. The results obtained (Figure 3) show that the retention of V(IV) increased up to pH 3 and remained practically constant at higher pHs. Nevertheless, the retention of V(V) increased up to pH 5 and decreased at higher pHs. Therefore, pH 5 was selected in this study as a compromise condition.

Other parameters studied were the NH_3 and HNO_3 concentration used to elute V(V) and V(IV), respectively. The concentrations studied varied from 0.01 to 0.2 M for NH_3 and from 0 to 0.4 M for HNO_3 . The volumes of NH_3 and HNO_3 used in this experiment were 6 and 10 mL, respectively. The results obtained (Figure 4) show that the integrated absorbance signal increased for V(V) up to 0.1M NH_3 and then

remained practically constant; therefore, this concentration was selected as the optimum concentration. Similar results were obtained for V(IV) by varying the HNO_3 concentration; therefore, 0.1M HNO_3 was chosen as the optimum concentration.

The next step was to study the influence of the volume of the eluting agent in the separation procedure. Therefore, experiments were performed varying the NH_3 volume from 4 to 10 mL and the HNO_3 volume from 6 to 12 mL. To compare the results obtained using the different volumes of NH_3 and HNO_3 ,

Figure 3. Influence of the pH of the sample.

Figure 4. Influence of the concentration of eluting agent in the V(IV) and V(V) separation.

the volume of each NH_3 extract was filled up to 10 mL with 0.1M NH_3 , and the volume of each HNO_3 extract was filled up to 12 mL with 0.1M HNO_3 . The volume of the extracting agent selected was 5 mL for 0.1M NH_3 and 8 mL for 0.1M HNO_3 .

Finally, the sample load flow rates and the eluting flow rates with NH_3 and HNO_3 were studied. The sample load flow rate was varied from 0.42 to 3.32 mL min^{-1} , and 0.83 mL min^{-1} was the selected for this study. The influence of the eluting flow rate with NH_3 and HNO_3 was studied ranging from 0.42–1.66 mL min^{-1} . For both cases, the optimum flow rate chosen was 0.83 mL min^{-1} .

Analytical Characteristics

Calibration graphs were measured using a synthetic seawater sample spiked with 0, 5, 7, and 15 $\mu\text{g L}^{-1}$ of both vanadium species. The solutions were subjected to the speciation procedure described in this work. The equations obtained were as follows:

$$\text{V(IV): } \text{QA} = 0.0026 + 0.0038 \text{ C;} \\ r = 0.9988$$

$$\text{V(V): } \text{QA} = 0.0032 + 0.0062 \text{ C;} \\ r = 0.9987$$

Where QA is the integrated absorbance signal, C is the vanadium concentration in $\mu\text{g L}^{-1}$, and r the linear regression coefficient.

Sensitivity was studied by means of two parameters: limit of detection (LOD) and limit of quantification (LOQ). Both the LOD and LOQ were calculated from 11 blank extract injections. The blank extracts of V(IV) and V(V), in HNO_3 and NH_3 , respectively, were obtained by passing 50 mL of a synthetic seawater sample through the column.

The LOD is defined as $3 \times \text{SD}/m$, where SD is the standard deviation of the measurements of the blank

and m is the calibration slope. The LOQ is defined as $10 \times \text{SD}/m$.

The instrumental LOD obtained was 1.5 $\mu\text{g L}^{-1}$ and the LOQ was 5 $\mu\text{g L}^{-1}$ for V(IV), and 0.75 $\mu\text{g L}^{-1}$ and 2.5 $\mu\text{g L}^{-1}$, respectively, for V(V). Taking into account the sample volume used, the LOD was 0.15 $\mu\text{g L}^{-1}$ and the LOQ was 0.50 $\mu\text{g L}^{-1}$ for V(IV), and 0.10 $\mu\text{g L}^{-1}$ and 0.33 $\mu\text{g L}^{-1}$, respectively, for V(V). The LOD and LOQ in seawater samples were found to be better than the limit obtained by Hayati Filik et al. (16) of 1.6 $\mu\text{g Kg}^{-1}$ for V(V). For groundwater, ZuLiang et al. (18) obtained 3 $\mu\text{mol L}^{-1}$ for V(IV) and 1 $\mu\text{mol L}^{-1}$ for V(V). However, the LODs obtained in this work were higher than the limits obtained by Shigeroni et al. (10) of 0.2 ng L^{-1} for V(V) determination in natural water by a catalytic method combined with solvent extraction and Chin-Chin Wann et al. (12) of 0.025 $\mu\text{g L}^{-1}$ for V(IV) and 0.041 $\mu\text{g L}^{-1}$ for V(V) using HPLC-ICP-MS.

The main advantage of our method is the speed and low cost of the analysis. The LODs obtained in this work can also be improved by using a higher volume of sample.

The repeatability of the overall procedure was calculated using a synthetic seawater sample spiked with 7 $\mu\text{g L}^{-1}$ of both species. Five portions of 50 mL of this sample were analyzed using the developed procedure. The RSDs obtained were 3.7% for V(IV) and 9.6% for V(V) which are values that are considered acceptable (<10%).

TABLE II
Recovery Percentages for
V(IV) and V(V) Determination

Vanadium Conc. ($\mu\text{g L}^{-1}$)	Recovery (%)	
	(IV)	(V)
5	96.8	93.0
7	91.7	89.4
15	97.2	94.5

The accuracy of the method was studied using the recovery percentages. Therefore, a seawater sample was spiked with 5, 7, and 15 $\mu\text{g L}^{-1}$ of both species and analyzed using this procedure. The results obtained are listed in Table II. The recovery percentages are between 91.7 and 97.2% for V(IV) and between 89.4, and 94.5% for V(V), with mean values of $95.3 \pm 3\%$ and $92.3 \pm 3\%$ for V(IV) and V(V), respectively. The recovery percentages are around 100%, thus the method is accurate.

Determination of Vanadium Species in Seawater Samples

The proposed method was applied to the determination of V(IV) and V(V) in seawater samples from the Arousa Estuary (Galicia, Northwestern Spain). The samples were collected using a Niskin bottle, filtered through 0.45- μm membrane filters, and stored at 4 °C prior to analysis. The samples were collected in triplicate and analyzed in triplicate. The results in Table III show that the V(IV) concentrations were lower than the detection limits in the three samples studied. The V(V) concentrations varied from 0.1 to 0.3 $\mu\text{g L}^{-1}$. These results agree with those obtained by Nakatsuka et al. (17) and Okamura et al. (11) for V(IV/V) determination in seawater samples who, however, only detected V(V) in the seawater samples analyzed.

TABLE III
Determination of V(IV) and V(V)
in Seawater Samples From Ría
de Arousa (Northwestern Spain)

Location	V(IV) ($\mu\text{g L}^{-1}$)	V(V) ($\mu\text{g L}^{-1}$)
Pobra de Caramiñal	<LOD	0.25 ± 0.01
Rianxo	<LOD	0.19 ± 0.03
Vilagarcía de Arousa	<LOD	0.10 ± 0.01

CONCLUSION

A simple, speedy, and low cost method for V(IV/V) determination in seawater samples was developed using a Chelex column and determination by electrothermal atomic absorption spectrometry (ETAAS). The method presents good precision [with RSDs of 3.7% for V(IV) and 9.6% for V(V)] and adequate sensitivity for the vanadium concentration levels present in seawater samples. The LODs were $0.15 \mu\text{g L}^{-1}$ and $0.10 \mu\text{g L}^{-1}$ for V(IV) and V(V), respectively. The limits of detection (LODs) can be improved by increasing the sample volume used for the analysis.

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