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Room temperature ionic liquid-based microextraction for vanadium species separation and determination in water samples by electrothermal atomic absorption spectrometry

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ABSTRACT

A simple microextraction technique based on room temperature ionic liquids (RTILs) for trace V(IV) and V(V) species separation and preconcentration in water samples was developed in this work. Vanadium species microextraction was achieved with a minimal amount of the RTIL 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) as vanadium-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (V-5-Br-PADAP) complex. The speciation analysis was performed based on a modern technique defined as temperature-controlled ionic liquid dispersive liquid phase microextraction (TILDLME). The level of V(IV) species was calculated by difference of total V and V(V) levels. Selectivity among V species was obtained with the use of 1,2-cyclohexanediaminetetraacetic acid (CDTA) as masking agent. Determination of V was developed by direct injection of the RTIL phase into the electrothermal atomic absorption spectrometer (ETAAS). A preconcentration factor of 40 was achieved with only 2 mL of sample. The limit of detection (LOD) obtained under optimum conditions was 4.9 ng L^{-1} and the relative standard deviation for 10 replicate determinations at the 0.5 μg L^{-1} V level was 4.3%, calculated at peak heights. A correlation coefficient of 0.9961 was achieved. The method was successfully applied for the speciation analysis of V in tap and river water samples.

1. Introduction

Bioavailability, accumulation and toxicological properties of V depend on the chemical forms in which it occurs. This metal can exist in many oxidation states (from −1 to +5), but the most common ones are +3, +4 and +5; as well as the oxyanions and oxycations, which are formed in solution [1]. For biological systems, water is one of the main sources of V, which is present in natural waters as V(IV) and V(V) inorganic species. The coexistence of these species depends on pH, redox potential and ionic strength of the aqueous media [2]. The distinction between these two V species is of particular interest due to differences in toxicity, being the vanadate ion more toxic than the vanadyl ion [3]. Although levels of up to about 70 μg L^{-1} have been reported in areas with high geochemical activity, most surface fresh waters contain less than 3 μg L^{-1} V [1]. Therefore, in order to achieve accurate, reliable and sensitive results, a separation and preconcentration step is often necessary prior to analysis.

Numerous separation and preconcentration techniques for the determination of V species have been proposed, including chelation and extraction [4], flotation [5], precipitation [6] and the use of ion-exchange [7] or chelating resins [8–11]. Also, V species have been studied using high-performance liquid chromatography, ion-exchange liquid chromatography and capillary electrophoresis [12–16]. Although liquid–liquid (L–L) solvent extraction can effectively decrease detection limits and eliminate matrix interference, the classical method requires large amounts of high purity organic solvents for the extraction. This high solvent consumption results in environmental and safety concern due to high volatility, toxicity and flammability [17]. Moreover, classical L–L extraction technique is often time-consuming, tedious and laborious [18]. Many of the problems associated to regular organic solvents as well as loss of solvent by evaporation can be avoided using ionic liquids (ILs) as alternative solvents, since they have no detectable vapour pressure and are relatively thermal stable even at elevated temperatures [19]. In the last few years, extractions of metal ions by using room

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temperature ionic liquids (RTILs) combined with complexing agents such as crown ethers, calixarenes and other organic ligands have been developed [19]. Hydrophobic RTILs form biphasic liquid systems with water, thus allowing extraction of low polar compounds from aqueous solution [20].

Solvent microextraction procedures based on RTILs have been reported for organic compound extractions, in which the volume of solvent required is significantly reduced while achieving high extraction efficiency [21]. Due to its large viscosity and undetectable volatility in comparison with conventional solvents, single-drop microextraction (SDME) and headspace microextraction (HSME) based on ILs have been proposed [19]. However, both methods are time-consuming, have limited reproducibility and presents some practical drawbacks such as the fact that the drop is broken up and air bubbles are formed when increasing agitation rate [22]. Temperature-controlled ionic liquid dispersive liquid phase microextraction (TILDLME) is a novel homogeneous L–L microextraction based on ILs developed for organic compounds and metal extraction, which avoids many of the problems of previous methods. Recently, Baghdadi and Shemirani have proposed the use of TILDLME for trace amounts of mercury extraction from several real water samples [22]. However, and to the knowledge of the authors, so far no analytical methods based on RTILs solvents have been developed for metal species determination.

The use of RTILs for extraction and separation in metal speciation analysis is for the first time reported in this work. Thus, an original method is proposed for preconcentration of V(IV) and V(V) species. The speciation analysis was developed with initial chelation of V species with the 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) reagent followed by TILDLME based on the RTIL 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]). The 5-Br-PADAP reagent has been successfully used as chelating agent for V [7], and its combination with [C_4mim][PF_6] has been reported for extraction and preconcentration of a different element [23]. However, RTILs-based extraction procedures have not been previously developed for elemental speciation analysis purposes. Selectivity of V species was achieved by using 1,2-cyclohexanediaminetetraacetic acid (CDTA) as masking agent for V(IV). Total V was determined after oxidation of V(IV) to V(V) with hydrogen peroxide. The levels of V(IV) species were calculated by difference of total V and V(V) levels. The proposed method was successfully applied to the determination of V(V) and V(IV) species at trace levels in natural and drinking water samples.

2. Experimental

2.1. Instrumentation

Elemental detection was performed using a PerkinElmer (Uberlingen, Germany) Model 5100ZL atomic absorption spectrometer equipped with a pyrolytic graphite tube (PerkinElmer) and a transversely heated graphite atomizer Zeeman-effect background correction system. A V hollow cathode lamp (PerkinElmer) operated at a current of 30 mA and a wavelength of 318.4 nm with a spectral bandwidth of 0.7 nm was used. All measurements were made based on absorbance signals with an integration time of 5 s. The temperature and time programmes for the atomizer are fully depicted in Table 1.

2.2. Reagents

Vanadium(V) stock standard solution, 1000 mg L^{-1}, was prepared by dissolving 2.2966 g of ammonium metavanadate (99.99%) (Merck, Darmstadt, Germany) in 1000 mL of ultrapure water. Lower concentrations were prepared by diluting the stock solution with 0.1 mol L^{-1} nitric acid.

Vanadium(IV) stock standard solution, 1000 mg L^{-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 sulphuric acid. Lower concentrations were prepared by diluting the stock solution with 0.1 mol L^{-1} nitric acid.

A 10^{-2} mol L^{-1} 5-Br-PADAP solution was prepared by dissolving 349.24 mg of reagent (Aldrich, Milwaukee, WI, USA) in 100 mL of ethanol. Lower concentrations were prepared by serial dilution with ethanol.

A 10^{-2} mol L^{-1} 1,2-cyclohexanediaminetetraacetic acid (CDTA) solution was prepared by dissolution of 364.35 mg CDTA·H_2O (Aldrich) in 100 mL of 0.1 mol L^{-1} sodium hydroxide (Aldrich) solution.

Acetic acid–acetate buffer solution was prepared from a 2 mol L^{-1} acetic acid solution adjusted to pH 4.75 by dissolution of sodium hydroxide.

A 50% (w/v) sodium nitrate solution was prepared by dissolving 5 g of $NaNO_3$ (Merck) in 10 mL of ultrapure water. For chemical modifier, a 1000 mg L^{-1} palladium nitrate solution was prepared by dissolving 106.6 mg $Pd(NO_3)_2$ (Merck) in 50 mL of 0.1% (v/v) HNO_3.

Ultrapure water (18 MΩ cm) was obtained from a Millipore Continental Water System (Bedford, MA, USA).

[C_4mim][PF_6] was synthesized according to a method proposed by Huddleston et al. [24] and stored in contact with ultrapure water to equilibrate the water content in the RTIL phase [25], qualitative analysis of synthesized IL was performed by comparison of infrared spectra with a commercially available [C_4mim][PF_6] (Solvent Innovation GmbH, Köln, Germany).

All glassware was acid washed with 10% (v/v) HNO_3 for at least 24 h and thoroughly rinsed five times with ultrapure water before use.

2.3. Sample collection and conditioning

For tap water samples collection, domestic water was allowed to run for 20 min and approximately a volume of 1000 mL was collected in a beaker. Tap water samples were analyzed immediately after sampling. River water samples were collected in cleaned bottles rinsed three times with water sample prior to collection. A sample volume of 1000 mL was collected at a depth of 5 cm below the surface. The river samples were filtered through 0.45 μm pore size membrane filters (Millipore Corporation, Bedford, MA, USA) immediately after sampling. As in natural waters V(IV) is oxidized slower at acid pH to V(V) than at higher pH [26], all samples were acidified to pH 1 with concentrated HNO_3 and stored at 4 °C in bottles (Nalgene; Nalge, Rochester, NY, USA). All the instruments used were previously washed with a 10% (v/v) HNO_3 water solution and then with ultrapure water.

2.4. General extraction and preconcentration procedure

A volume of 45 μL [C_4mim][PF_6] was added into a 10 mL glass marked conical tube with 2 mL of sample, 100 μL ethanol, 200 μL of 10^{-3} mol L^{-1} 5-Br-PADAP solution and 10 μL of 2 mol L^{-1} (pH 4.75) acetate/acetic acid buffer. For optimization procedures, 2 mL of 2.5 μg L^{-1} V(IV) or V(V) standard solution was used instead of water sample. Firstly, the tube was shaken with a vortex stirrer obtaining a dispersion of the RTIL into the aqueous media. Then, the mixture was heated in a thermostated bath at 60 °C for 4 min to fully dissolve the RTIL phase. Secondly, the homogeneous solution was placed in an ice bath for 10 min and a cloudy solution was thus formed, extracting the V-5-Br-PADAP complex into the RTIL phase. Finally, centrifugation at 1500 rpm (302 g) for 15 min allowed the formation of two well-defined phases. The upper aqueous phase

Table 1
Instrumental and experimental conditions for V species determination.

Instrumental conditions	
Wavelength	318.4 nm
Spectral band width	0.7 nm
Lamp current	30 mA
Injecting volume	50 μL
Modifier volume	11 μL
Modifier mass	5 μg Pd

Graphite furnace temperature program

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min^{-1})
Drying 1	110	1	30	250
	30	10	20	250
Drying 2	150	99	10	250
Drying 3	600	10	10	250
Drying 4	800	5	10	250
Pyrolysis	1800	20	20	250
Atomization	2500	0	3	–
Cleaning	2600	1	2	250

Extraction conditions	
Working pH	4.75
Sample volume	2 mL
5-Br-PADAP concentration	10^{-4} mol L^{-1}
Ethanol concentration	5% (v/v)
Buffer concentration	5×10^{-3} mol L^{-1}
Volume of RTIL	45 μL
Heating temperature	60 °C
Heating time	4 min
Cooling time	10 min
Centrifugation time	15 min ($302 \times g$)

was manually removed with a syringe and the RTIL phase was dissolved with 50 μL of methanol before it was directly injected into the graphite furnace for V determination (Table 1). The procedure was selective of V(V) species with 10 μL of 10^{-2} mol L^{-1} CDTA added as masking reagent for V(IV) species. After oxidation of V(IV), total V was determined as described above. Thus, concentration of V(IV) species was calculated as the difference between the total concentration of V and that of V(V). Calibration was performed against aqueous standards submitted to the same preconcentration procedure. Likewise, blank solutions were analyzed similarly to standard and sample solutions.

2.5. Oxidation of V(IV) species

Hydrogen peroxide was used for oxidation of V(IV) to V(V) species. A standard solution (2.5 μg L^{-1} V(IV)) volume of 70 mL was added with 500 μL of 100 vol. hydrogen peroxide. Five minutes after, the solution was boiled on a heating plate for 15 min in order to remove any excess of hydrogen peroxide. After this procedure, the resulting solution was cooled to room temperature and then taken up to 100 mL with ultrapure water. A similar oxidation procedure was applied to samples for total V determination and before IL-based microextraction.

3. Results and discussion

3.1. Optimization of vanadium extraction conditions using [C_4mim][PF_6]

Due to the high polarity of V ions, their extraction efficiency by the sole application of [C_4mim][PF_6] could be too low. In order to increase the extraction efficiency of metal ions it is necessary to improve their affinity for the RTIL phase by complexing with a suitable reagent such as 5-Br-PADAP [25]. The effect of 5-Br-PADAP concentration on the analytical signal was evaluated. It was observed that V extraction improved by increasing the 5-Br-PADAP concentration up to 10^{-4} mol L^{-1}. No mayor changes were observed when higher concentrations of 5-Br-PADAP were employed. Thus, 10^{-4} mol L^{-1} 5-Br-PADAP was chosen as the optimum.

The pH of media plays an important role on metal–chelates formation and subsequent extraction because it defines the charge of the complex, thus determining its extraction efficiency. In this experiment, the effect of pH on the extraction performance was studied within the range of 2.5–7.5 by adding appropriate volumes of HCl or NaOH solution to the samples. Results are shown in Fig. 1 (for all figures in this work, the term "relative response" is defined as the percent of each value with respect to the highest value of the variable under study). It was observed that the optimum pH was in the interval of 3.5–5. Therefore, samples and standards were

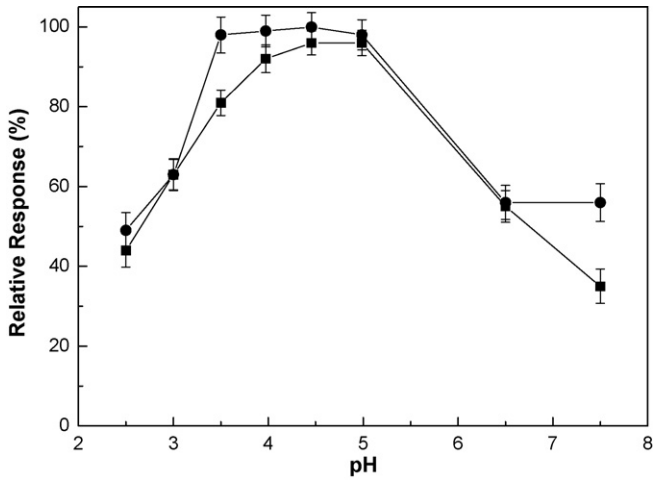

Fig. 1. Effect of pH on V species extraction and preconcentration. Vanadium (IV) (■); vanadium (V) (●). Other conditions were as indicated in Table 1.

adjusted at pH 4.75 before extraction. At this pH value, a neutral 5-Br-PADAP chemical form is obtained, as deduced from the dissociation constants of the reagent (pK_{a1} = 0.1, pK_{a2} = 2.02 and pK_{a3} = 11.30) [27]. In order to maintain a constant working pH that allows complex formation and stability, an acetic/acetate buffer solution was selected. The possible influence of buffer concentration on analyte extraction was studied in the range of 5×10^{-3} to 0.1 mol L^{-1}. A concentration of 5×10^{-3} mol L^{-1} was chosen for subsequent experiments while a drop in the extraction efficiency was observed upon an increase in buffer concentration. This behaviour could be due to ionic strength effect on complex extraction by the RTIL phase. Future studies will be developed to explain this effect.

The V-5-Br-PADAP complex precipitates in aqueous medium due to its low polarity, negatively affecting the extraction efficiency of the technique. To avoid this effect, ethanol was added to the sample solution as a solubilization medium. Ethanol concentration effect was studied in the range of 1-10% (v/v). It was observed that V-5-Br-PADAP complex precipitated for ethanol concentrations lower than 1% (v/v). However, in the range of 1–5% (v/v), no changes in the analytical signal were observed and the complex was kept in solution, while achieving the highest extraction efficiency. Therefore, 5% (v/v) was chosen for subsequent experiments. Higher ethanol concentrations led to a drop in analytical signal. This effect could be due to a higher solubilization of the RTIL by ethanol. On the other hand, no effect on the kinetics of phase separation and extraction was observed with ethanol.

Generally, the addition of salt in traditional liquid–liquid extraction using conventional organic solvents often increases the extraction performance due to salting out effect. This effect was investigated on the method over a $NaNO_3$ concentration range of 0–8% (w/v). As expected, the response was slightly increased as a result of salting out effect in the range of 0–1% (w/v) $NaNO_3$. The analyte extraction decreased for salt concentrations beyond 1% (w/v) and reached a minimum at 4% (w/v) $NaNO_3$. It was also observed that some of the RTIL phase was solubilized into the aqueous phase with an excessive amount of salt added to the extraction system. This behaviour has been reported previously for ionic liquid-based LPME [18,22,28]. Thus, salt addition was not adopted as it would significantly affect the formation of the biphasic system.

The complete solubilization and dispersion of $[C_4mim][PF_6]$ into the aqueous solution depends on temperature, playing an important role in this method [29]. Before shaking, the RTIL-containing solutions were heated in the range of 50–90 °C. However, the best analytical signal was obtained in the range of 60–80 °C. It was observed that total solubilization of the RTIL phase was achieved from 60 °C. Therefore, this temperature was selected for the heating step during the extraction procedure. The effect of heating time on V species extraction by the RTIL phase was also studied (Fig. 2). The best results were obtained when the solution was placed for 4 min in the hot bath. Regarding the extraction time, this was considered from the moment the tube containing the RTIL-aqueous phase homogenous solution was put into an ice water bath to the set interval. The turbidity phenomenon, as a result of decreasing RTIL solubility, not only was easy to generate when cooling with ice water, but also this step led to lower times for phase separation. The best results were obtained for 5 min. No changes were observed when solutions were cooled for longer times.

Centrifugation controls the complete and fast phase separation. With short centrifuging times, total phase separation was not achieved and very small drops of $[C_4mim][PF_6]$ were observed still in suspension. On the other hand, longer centrifuging times resulted in temperature increasing, leading to a higher dissolution of the IL phase and diminishing analyte extraction. Different centrifugation times were evaluated at 1500 rpm (302 × *g*). A higher centrifugation speed compromised the structural integrity of the glass tubes.

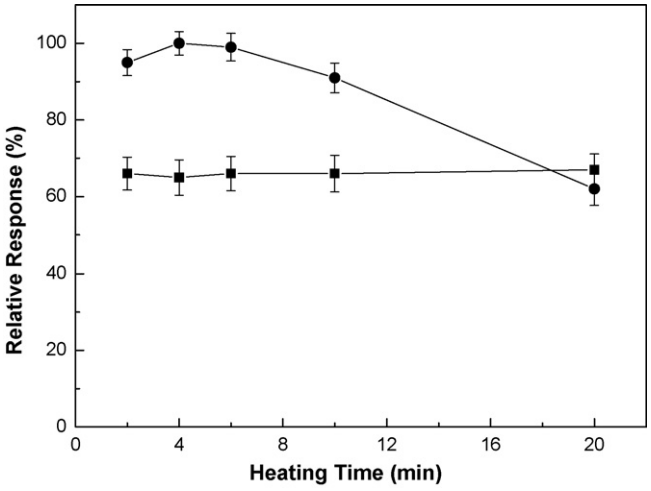

Fig. 2. Influence of heating time of the RTIL-based system on V species extraction. Vanadium (IV) (■); vanadium (V) (●). Other conditions were as indicated in Table 1.

Thus, a centrifugation time of 15 min resulted to be optimum for complete RTIL phase separation.

3.2. Masking reagent effect and selectivity of vanadium species

As a result of the optimization of extraction and complexes formation conditions, different extraction efficiencies were obtained for V(V) and V(IV) species. However, complete separation of V species was not achieved at this point of the work and hence, an alternative approach had to be pursued for selective extraction. The CDTA reagent has already been used as masking agent avoiding V(IV) species to form a complex with the 5-Br-PADAP reagent [7]. In Fig. 3 is shown the masking effect of CDTA on V(IV) extraction with the RTIL-based biphasic system. A concentration of 5×10^{-5} mol L^{-1} CDTA allowed total masking of V(IV) species. It was also noticed, that the addition of CDTA to the system reduced the extraction (from 99 to 75%) of V(V) species as compared to those experiments without CDTA. This effect was not observed before, when V-5-Br-PADAP complexes were retained on an Amberlite XAD-7 in a solid phase extraction system [7]. Thus, this anomalous behaviour could be explained due to an interference effect of CDTA over the extraction mechanism of V(V)-5-Br-PADAP with the RTIL phase. Certainly, this effect will be a matter of future studies.

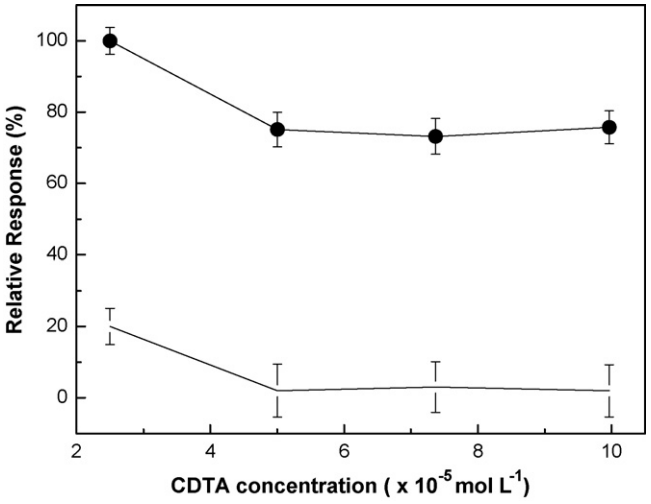

Fig. 3. Effect of CDTA concentration on V species selectivity and separation. Vanadium (IV) (■); vanadium (V) (●). Other conditions were as indicated in Table 1.

Table 2
Selectivity of the method for V(IV) and V(V) species determination.

	V(IV)			V(V)		
V(IV)/V(V) ratio	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)
0.2	0.50	0.49	98.0	2.5	2.55	102.0
1	1.5	1.48	98.7	1.5	1.46	97.3
5	2.5	2.54	101.6	0.5	0.5	100.0

3.3. Study of ETAAS conditions for V determination in RTIL phase

Due to the high viscosity of the resulting RTIL phase, its direct automatic injection into the ETAAS furnace imposes some drawback. In order to inject the RTIL phase into the graphite furnace in a reproducible manner, it was previously dissolved in an appropriated solvent. Dilution of the RTIL phase in different organic solvents (ethanol, acetone, or methanol) was assayed in this work. While dilution of the RTIL phase in all these solvents was feasible, the best absorbance signal was obtained by using methanol as diluent. Thus, methanol was chosen for further experiments.

An increase of the background signal during the atomization step was observed in presence of the RTIL, due to its organic nature. Since background correction is more accurate when background absorbance is small with respect to the atomic absorption signal, the study was focused on matrix elimination before the atomization step. An *in situ* digestion was developed by injecting different amounts of H_2O_2 or HNO_3 after the evaporation step and development of diverse temperature ramps in the pyrolysis step. Optimal results were obtained when 10 μL of H_2O_2 30% (v/v) were injected during the second 30 °C drying step used in the graphite furnace program (Table 1), and before temperature ramps in the pyrolysis process were initiated. Despite the background reduction, a minimal reduction in the analytical signal of V in presence of RTIL was also observed. Moreover, as the concentration of RTIL increased, V absorbance gradually decreased. During RTIL thermal decomposition, fumes were produced to some extend, which probably resulted in loss of V in the ashing stage. Additionally, direct formation of fluoride volatile species of V, with HF occurring from $[C_4mim][PF_6]$ thermal decomposition [30], could be considered to explain this phenomenon. Calibration curves for V determination by ETAAS were obtained in presence and absence of the RTIL phase. Thus, a reduction in analytical sensitivity was found for increasing amounts of the RTIL phase injected into the graphite furnace. For improvement of V signal, different amounts of $NH_4H_2PO_4$, $Mg(NO_3)_2$, $Pd(NO_3)_2$ and mixtures of them were tested as chemical modifiers. A signal improvement was observed when 5 μg of Pd were injected into the furnace. No improvements were observed when a permanent Pd-modified graphite tube was employed. Thus, Pd injected before the sample was used in subsequent work as chemical modifier.

Finally, a study was developed to fully evaluate the effect of the RTIL on the analyte measurement by ETAAS. Thus, a 50 $\mu g\,L^{-1}$ V solution in same conditions as resulting from extraction procedure, and with equal amount of the RTIL $[C_4mim][PF_6]$, was used for optimization of pyrolysis and atomization steps. The optimum pyrolysis temperature was selected by studying the absorption to background signals ratio and peak shape. Well defined Gaussian and sharp peaks were considered as optimal. For temperature values higher than 1800 °C, analyte loss was evidenced during pyrolysis (Fig. 4). On the other hand, no signal was observed when this temperature was assayed in the atomization step. Therefore, 1800 °C was chosen as the pyrolysis temperature for further determinations. Once selected pyrolysis temperature, the effect of atomization temperature on V signal was studied within the range of 2200–2500 °C. The maximum signal was obtained at 2500 °C in maximum power mode and under stop flow conditions (Fig. 4). ETAAS final conditions are shown in Table 1.

3.4. Interferences study

The effect of concomitant ions regularly found in natural water samples was evaluated by analyzing 2 mL of 2.5 $\mu g\,L^{-1}$ V solution containing concomitant ions at different concentrations, and following the recommended extraction procedure. Thus, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+} could be tolerated up to at least 2000 $\mu g\,L^{-1}$. Commonly encountered concomitant ions such as alkali and alkaline earth elements do not form stable complexes with 5-Br-PADAP at working pH. On the other hand, 5-Br-PADAP reagent forms stable complexes with various elements (including Ca^{2+} and Mg^{2+}), but only at elevated pH values. Contribution to the ionic strength of the system was insignificant and did not affect the extraction efficiency. Analytical signal of the blank was not modified in presence of the concomitant ions assayed. As expected, humic substances do not produce interference effects on analyte extraction with imidazolium hexafluorophosphate-type RTILs [31].

3.5. Analytical performance

An extraction percentage of about 75% was achieved when the procedure was carried out under the optimum experimental conditions (Table 1). The overall extraction efficiency (E) was calculated according to the following equation [32,33]:

$$E = \frac{C_{RTIL} \times V_{RTIL}}{C_i \times V_{FA}}$$

where C_i is the initial concentration of V in the aqueous phase before extraction, C_{RTIL} is the final concentration of V in the RTIL phase, V_{FA} and V_{RTIL} are the volume of aqueous and RTIL phase, respectively. The obtained sensitivity enhancement factor for a sample

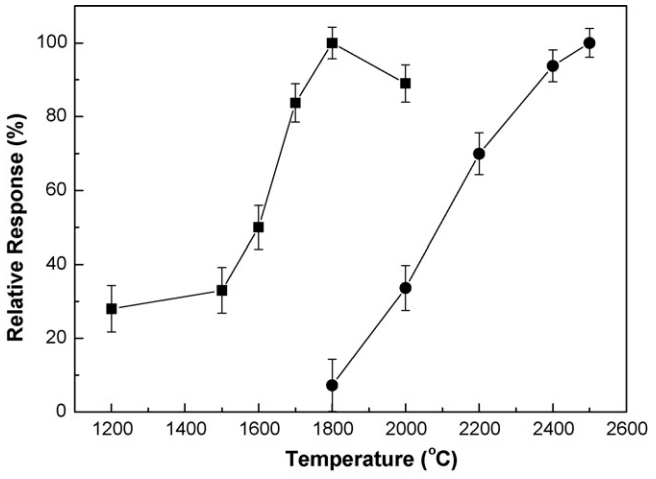

Fig. 4. Pyrolysis (■) and atomization (●) temperature curves for 50 $\mu g\,V\,L^{-1}$ in presence of 9.8×10^{-2} mol L^{-1} 5-Br-PADAP, RTIL-methanol and 5 μg of Pd as modifier. Atomization temperature for pyrolysis optimization: 2500 °C. Pyrolysis temperature for atomization optimization: 1800 °C.

Table 3
Concentrations of V(IV) and V(V) in river and tap water samples (95% confidence interval; $n = 6$).

	Sample	V(IV)			V(V)		
		Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)[a]	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)[a]
River water	1	0	0.38 ± 0.02	–	0	0.98 ± 0.05	–
		1.25	1.64 ± 0.06	100.8	1.25	2.24 ± 0.12	100.8
	2	0	0.46 ± 0.03	–	0	0.85 ± 0.05	–
		1.25	1.68 ± 0.08	97.6	1.25	2.11 ± 0.10	100.8
	3	0	0.54 ± 0.03	–	0	1.88 ± 0.08	–
		1.25	1.79 ± 0.09	100.0	1.25	3.12 ± 0.17	99.2
	4	0	0.73 ± 0.05	–	0	1.59 ± 0.06	–
		1.25	2.00 ± 0.11	101.6	1.25	2.91 ± 0.16	105.6
Tap water	1	0	0.14 ± 0.02	–	0	1.05 ± 0.06	–
		1.25	1.40 ± 0.06	100.8	1.25	2.32 ± 0.11	101.6
	2	0	0.10 ± 0.01	–	0	1.63 ± 0.08	–
		1.25	1.39 ± 0.09	103.2	1.25	2.84 ± 0.17	96.8
	3	0	0.09 ± 0.01	–	0	0.98 ± 0.05	–
		1.25	1.33 ± 0.06	99.2	1.25	2.22 ± 0.12	99.2
	4	0	0.17 ± 0.02	–	0	0.67 ± 0.03	–
		1.25	1.43 ± 0.06	100.8	1.25	1.94 ± 0.09	101.6

[a] [(Found-base)/added] × 100.

volume of 2 mL was 40. The enhancement factor was calculated as the slopes ratio of the calibration curve for V with and without the extraction/preconcentration step [34]. The relative standard deviation (RSD) resulting from the analysis of 10 replicates of 2 mL solution containing 0.5 $\mu g\,L^{-1}$ V(V) was 4.3%. The calibration graph was linear with a correlation coefficient of 0.9961 at levels near the detection limits and up to at least 5000 $ng\,L^{-1}$. The limit of detection (LOD) was calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve [35]. A LOD of 4.9 $ng\,L^{-1}$ was obtained for the proposed methodology. Finally, in order to allow V species determination by difference between the total V content and that of V(IV), CDTA reagent was added to all solutions. Therefore, an extraction of 75% for V was achieved for both situations and then only one calibration curve was needed.

3.6. Vanadium speciation analysis in water samples

In order to assess the selectivity of the proposed method on V(IV) and V(V), it was applied to various synthetic samples with different concentration ratios between the two oxidation states. It can be observed in Table 2, that both V species were completely separated and quantitatively recovered. The method was thus shown to have an acceptable accuracy under different conditions, with recovery percentages between 97.9 and 101.6% for V(IV) and between 97.7 and 101.9% for V(V).

The most commonly found oxidation states in sufficiently aerated waters are V(IV) and V(V) [2], and the highest proportion of V corresponds to soluble forms [6]. Taking this into account, the proposed method was applied to the determination of soluble V(IV) and V(V) in several tap and river water samples. The results are shown in Table 3. The concentrations in river water samples were in the range 0.38–0.73 $\mu g\,L^{-1}$ for V(IV) and 0.85–1.25 $\mu g\,L^{-1}$ for V(V). The concentrations of V species in tap water were in the range of 0.09–0.17 for V(IV) and 0.67–1.23 for V(V). Results are in good agreement with a previous work, where similar V(IV) and V(V) concentrations in water samples were reported [7].

4. Conclusions

The novel use of RTIL-based L–L microextraction procedures for trace element speciation analysis is for the first time reported in this work. This study indicates that temperature-controlled ionic TILDLME can be an excellent and green extraction technique for V species separation and preconcentration. Moreover, the amount of an organic solvent required for the extraction procedure is significantly reduced by employing the TILDLME technique. Therefore, a simple as well as environmentally friendly analytical methodology is achieved. Direct analysis and accurate determination of V species by ETAAS are demonstrated even in the presence of the complex organic matrix of the solvent. Likewise, Pd was a feasible matrix modifier for direct V determination in RTIL phase. Compared to indirect methods, the proposed method offers the advantages of rapidity and simplicity. The proposed method presents a detection limit that is comparable to, or better than, other methodologies developed for V species determination (Table 4), and has good calibration range with a reduced amount of sample. Moreover, the detection limits obtained by the proposed methodology allowed the determination of V species at trace levels with good reproducibility and accuracy both in synthetic and real water samples. Therefore, the method could be of key interest especially for routine analytical laboratories.

Table 4
Characteristic performance data obtained by using the proposed method and others reported for V species determination in water.

Method	LOD ($ng\,L^{-1}$)	RSD (%)	Sample consumption (mL)	Calibration range ($ng\,L^{-1}$)	Ref.
LC-USN-ICP-MS	25 V(IV); 41 V(V)	5.6 V(IV); 2.3 V(V)	0.1	0.1–20	[36]
SPE-Spectrophot.	16 V(IV); 14 V(V)	4.7 V(IV); 4.0 V(V)	250	1.4–150	[37]
SPE-CE-UV	3 $mol\,L^{-1}$ V(IV); 1 $mol\,L^{-1}$ V(V)	0.65–1.23	[b]	5.1×10^2 to 1.5×10^4	[38]
SPE-ASCFA[a]	[b]	1.1 V(IV); 0.9 V(V)	3	2.51–765	[39]
FI-USN-ICP-OES	19	2.3	10	1000	[7]
SPE-ETV-ICP-OES	0.68	4.8 V(IV); 4.3 V(V)	5	6.8–1000	[40]
FIA-Spectrophot.	101.0 V(IV); 151.6 V(V)	1.09 V(V); 1.23 V(IV)	0.4	5.1×10^2 to 1.02×10^6	[41]
TILDLME-ETAAS	4.9 V(V)	4.3 V(V)	2	5000	Proposed method

[a] Air-segmented continuous flow analysis (ASCFA).
[b] Non-reported.

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