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Speciation of vanadium in water with quinine modified resin micro-column separation/preconcentration and their determination by fluorination assisted electrothermal vaporization (FETV)–inductively coupled plasma optical emission spectrometry (ICP-OES)

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Abstract

A simple and selective method of flow injection (FI) using a micro-column packed with quinine modified resin as solid phase extractant has been developed for preconcentration and separation of trace amount of vanadium(V) and vanadium(IV) in water samples, followed by determination with fluorination assisted electrothermal vaporization (FETV)–inductively coupled plasma optical emission spectrometry (ICP-OES). At pH 3 ∼ 3.8, the modified resin is selective towards V(V) and almost not towards V(IV), while, V(IV) could be quantitatively adsorbed by the modified resin at pH 5 ∼ 7. The two vanadium species adsorbed by modified resin could be readily desorbed quantitatively with 0.3 ml of 0.5 mol l^{-1} HCl. Both vanadium species in elution were then determined by ETV–ICP-OES with the use of polytetrafluoroethylene (PTFE) as chemical modifier. Effects of acidity, sample flow rate, concentration of elution solution and interfering ions on the recovery of the analytes have been systematically investigated. Under the optimal conditions, the adsorption capacities of the quinine modified resin for V(V) and V(IV) are 7.6 and 8.0 mg g^{-1}, respectively. The detection limit (3σ) of V is 0.072 ng ml^{-1} for FETV–ICP-OES and 0.56 pg ml^{-1} for FETV–ICP-MS with enrichment factor of 62.5, and the relative standard deviation (R.S.D.) is 4.9% ($n = 9$, $C = 0.2$ μg ml^{-1}) and 3.8% ($n = 9$, $C = 1.0$ ng ml^{-1}), respectively. The proposed method has been applied to the determination of trace V(V) and V(IV) in different water samples, and the recoveries of V(V) and V(IV) are 100 ± 10%. In order to further verify the accuracy of the developed method, FETV–ICP-MS was employed to analyze the vanadium species in water samples after separation/preconcentration, and analytical results are in good agreement with that obtained by the proposed method. The developed method was also applied to the analysis of the total V in GBW07401 soil certified reference material and in GBW07605 tea leaves certified reference material, and the determined values coincided with the certified values very well.

Keywords: Vanadium(V); Vanadium(IV); Quinine modified resin; Preconcentration and separation; FETV–ICP-OES; Polytetrafluoroethylene; Chemical modifier

1. Introduction

The chemical and biological properties of an element depend very much on its oxidation state, hence an accurate determination of different species of a given element is important for evaluating the comprehension of its biological and physiological functions, as well as potential toxicity. Vanadium has various oxidation states and ionic forms in aqueous solution. It is indispensable to the growth of biology at μg ml^{-1} level, and however, much higher content of V shows toxic properties [1] with V(V) being more toxic than V(IV) [2]. Therefore, differentiation and quantification of vanadium in these two oxidation states are important [3,4].

In natural water samples, the existing oxidation states of vanadium are mainly V(V) and V(IV) [2], and its concentra-

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tion in these samples was estimated at the level of ng ml^{-1} [5,6]. Due to the extreme low concentration of vanadium in real samples and severe matrix interference existed in determination, highly sensitive and selective analytical techniques are needed. Furthermore, an effective separation and preconcentration procedure is also usually indispensable to differentiate between V(V) and V(IV).

The most widely used techniques for the separation and preconcentration of vanadium include liquid–liquid extraction [3], coprecipitation [7] and ion exchange and sorption [8–18]. Among these techniques, the methods using ion exchange resins or sorbent extraction have proved to be especially effective. By using Chelex 100 resin, Soldi et al. [11] developed a method for separation of V(V) and V(IV). This method consists of sorbing both V(V) and V(IV) at a pH of about 4.5, and separating them by stripping V(V) at basic condition (pH 10) and then V(IV) at acidic condition (pH 0.8). Also, an imidazole 4,5-dicarboxylic acid resin was adopted by Banerjee et al. [12] for sorbing both V(V) and V(IV) at a pH of 3.0, and V(IV) get eluted by malonic acid, while V(V) by NaOH solution. In recent years, pre-column derivation and modifying the support material with chemical and physical method [13] are mainly adopted as an effective measure to realize the speciation of vanadium in various samples. The on-line formation of V-5-Br-PADAP complexes together with the use of cychohexane–diamine–tetraacetic acid (CDTA) as a masking agent and XAD-7 resin was developed by Wuilloud et al. [13] for the separation and determination of V(V) and V(IV). Minelli et al. [14] used a suitable strong anionic exchange column (SAX) loaded with disodium ethylendiaminetetraacetic acid (Na_2EDTA) to trap both vanadium species at pH 3, and V(IV) was selectively eluted by means of the mixture solution of Na_2EDTA, tetrabutylammonium hydroxide (TBA^+OH^-) and isopropanol (^{i}Pr–OH). However, the above two methods [13,14] cannot determine the two vanadium species successively, the concentration information on the second vanadium species was obtained by subtracting the first vanadium species concentration from the total concentration of vanadium. Okamura et al. [15] proposed a method for successively measuring V(V) and V(IV) in water samples by using acetylacetone and 8-quinolinol immobilized on partiallyfluorinated silicon alkoxide glass column. Although the stability of the extractant obtained by immobilizing chelating reagent into a support material is not so good, the simplicity to prepare, easiness to obtain and cheapness still drew extensive interest in analytical atomic spectroscopy for trace analysis and speciation studies.

Several analytical techniques, such as neutron activation analysis (NAA) [19,20], atomic absorption spectrometry (AAS) [21], inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) [13,22], have been applied to accurately determine trace vanadium and its species in various samples. It should be noted that electrothemal vaporization (ETV)–ICP-OES, as an effective trace detection technique, has the merits of high sensitivity, low sample consuming, simple to operate, reduced matrix effect, high intake efficiency and directly analysis of solid sample, and thus, gets extensive applications in trace element analysis [23,24]. In recent years, special attention has been paid to the improvement of the analytical performance of this technique for determination of refractory elements by exploring various chemical modifiers. Of all chemical modifiers, halogenating reagents, especially polytetrafluoroethylene (PTFE), has been proven to be very effective to suppress the formation of refractory carbides, to eliminate the memory effect, and therefore, to improve the analytical performance of the method [25]. In our previous study [25], a slurry sampling fluorination assisted electrothermal vaporization (FETV)–ICP-OES method using PTFE slurry as the chemical modifier was reported for the determination of V in environmental materials.

In the field of the resolution of chiral analytes, some alkaloids, especially cinchona alkaloids, such as quinine and quinidine, and their derivatives, have been extensively used as anion exchanger type selectors in different separation techniques. Quinine belongs to the quinoline alkaloids with antimalarial activity that forms complexes with certain heavy metal ions due to its amino group, which can transform into $R_3HN^+{-}Cl^-$ in HCl media, and thus like conventional anion exchanger, can exchange with anion complexes of metals. A resin made by immobilizing alkaloid quinine onto a suitable solid support may show the characteristics of quinine.

The aim of this work was to prepare a new kind of extractant by immobilizing alkaloid quinine onto the weakly acidic cation exchange resin, and to develop a sensitive and simple method for the speciation of vanadium (V/IV) using the quinine modified resin separation/preconcentration and their successive determination by FETV–ICP-OES. The retention and elution conditions for fractionalization and preconcentration of V(V) and V(IV) have been studied and the optimized experimental conditions were established. The developed method was applied to the determination of two vanadium species in nature water with satisfactory results.

2. Experimental

2.1. Apparatus

The graphite furnace sample introduction device and ICP-OES instrument used in this work were identical with that reported previously [24]. An ICP spectrometric system (Beijing Broadcast Instrument Factory, Beijing, China) with 2-kW plasma generator was used with a conventional quartz torch. A WF-1B type heating device with a matching graphite furnace (Beijing Second Optics, Beijing, China) was used for analyte vaporization. The radiation from the plasma was focused as a 1:1 image on the entrance slit of a WDG 500-1A type monochromator (Beijing Second Optics) having a reciprocal linear dispersion of 1.6 nm mm^{-1}. The transient emission signals from plasma were detected with a R456 type photomultiplier tube (Hamamatsu, Japan) fitted with a

Table 1
ETV–ICP-OES and ETV–ICP-MS operating conditions

Parameters	
ICP-AES	
Wavelength (nm)	V: 310.2
Incident power (kW)	1.0
Carrier gas (Ar) ($l\,min^{-1}$)	0.6
Coolant gas (Ar) ($l\,min^{-1}$)	16
Plasma gas (Ar) ($l\,min^{-1}$)	0.8
Observation height (mm)	12
Entrance slit-width (μm)	25
Exit slit-width (μm)	25
Plasma condition	**Ion lenses**
ICP-MS	
RF Power: 1250 W	Extract 1: −164 V
RF matching: 1.58 V	Extract 2: −93 V
Sampling Depth: 6.8 mm	Einzel 1, 3: −100 V
Carrier Gas: 1.15 $l\,min^{-1}$	Einzel 2: 10 V
PeriPump: 0.1 rps (0.4 $ml\,min^{-1}$)	Plate bias: −4 V
RF Power: 1250 W	Extract 1: −164 V
RF matching: 1.58 V	Extract 2: −93 V
ETV	
Drying temperature (°C)	100; ramp 10 s, hold 10 s
Ashing temperature (°C)	800; ramp 15 s, hold 15 s
Vaporization temperature (°C)	2340, 4 s
Clearing temperature (°C)	2600, 2 s
Sample volume (μl)	10

laboratory-built direct current amplifier, and recorded by a U-135C recorder. An Agilent 7500a ICP-MS (Agilent, Japan) with ETV sample introduction unit is used to verify the accuracy of the developed method. The ETV device and its conjunction with ICP-MS were described in reference [26]. The used instrument operating conditions for ETV–ICP-OES and ETV–ICP-MS are given in Table 1.

A SY 1200 type ultrasonic instrument (Shanghai Shengyuan Ultrasonic Instrument Equipment Corporation, Shanghai, China) was used for the preparation of quinine modified resin and the slurry samples.

The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments (Shanghai) Co. Ltd.) supplied with a combined electrode.

A HL-2 peristaltic pump (Shanghai Qingpu Instrument Factory, China) was used in separation and preconcentration process. A minimum length of PTFE tubing (i.d. 0.5 mm) was used for flow injection (FI) connections. A self-made PTFE microcolumn (20 mm × 3.0 mm i.d.) was used.

2.2. Standards solutions and reagents

The V(IV) and V(V) stock solutions (1.000 $mg\,ml^{-1}$) were prepared by dissolving of high purity $VOSO_4$ and NH_4VO_3 (The first Reagent Factory, Shanghai, China) in 0.01 $mol\,l^{-1}$ sulfuric acid containing 0.1 $\mu mol\,l^{-1}$ ascorbic acid and 0.01 $mol\,l^{-1}$ hydrochloric acid, respectively. Analytical mixture standard solutions of V(V) and V(IV) were prepared by mixing and diluting the stock solutions. All other reagents used were of analytical reagent grade. Doubly distilled water was used throughout.

Twenty grams of commercial #724 weakly acidic cation exchange resin (Hangzhou Zhengguang Resin Ltd., Hangzhou, P.R. China), with 200–300 mesh size, was immersed in 50 ml of 0.5 $mol\,l^{-1}$ NaOH and 50 ml of 3.0 $mol\,l^{-1}$ HCl for 24 h, respectively, filtered and washed with doubly distilled water until neutral, then dried prior to storage for use in preparation of the quinine modified resin.

2.3. Preparation of quinine modified resin

For the preparation of quinine modified resin, 65 ml of 1% (v/v) sulfuric acid solution was used to dissolve 0.82 g quinine before 5 g cation exchange resin was added, and the resulting mixture was finally stirred ultrasonically for 1 h, and deposited overnight. Then the quinine modified resin was filtered, washed with doubly distilled water until neutral, dried at 60 °C in a vacuum dryer prior to storage for use in the separation of the V species.

2.4. Column preparation

A total of 50 mg of quinine modified resin was filled into a PTFE micro-column (20 mm × 3.0 mm i.d.), plugged with a small portion of glass wool at both ends. The column was conditioned to the desired pH with 0.1 $mol\,l^{-1}$ HCl–NaAc solution.

2.5. Slurry sample preparation

For the determination of the V species, 40 μl 60% PTFE emulsion was added to 300 μl sample, and diluted to 400 μl with doubly distilled deionized water. The aqueous standard solution series containing 6% (w/v) PTFE was used for calibration. The resulting mixtures were dispersed with an ultrasonic vibrator for 15 min and the bottles shaken prior to sampling.

2.6. Sample pretreatment

2.6.1. Water samples

Lake water (pH 9.4) (East Lake Wuhan, China) and Tap water was collected. Immediately after sampling, the samples were filtered through a 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China) prior to analysis. Suitable amounts of 1.0 $mol\,l^{-1}$ HCl were added to adjust the acidity of samples. The samples were stored at 4 °C in low-density polyethylene (LDPY) bottles when the analysis of water samples was not carried out. The storage period was kept as short as possible.

2.6.2. Biological and environmental sample analysis

Tea leaves (GBW07605) (0.2000 g) were weighed and dissolved in 15 ml of HNO_3–$HClO_4$ (4:2, v/v) on a hot plate

under mild heating and vaporized to near dryness, and finally dissolved in 10 ml of pH 3 HCl–NaAc buffer solution.

Soil (GBW07401) (0.0200 g) were weighed and dissolved in 10 ml of HNO_3–$HClO_4$–HF (4:2:1, v/v/v) on a hot plate under mild heating and vaporized to near dryness, and finally dissolved in 10 ml of pH 3 HCl–NaAc buffer solution.

2.7. Recommended procedures

2.7.1. Separation/preconcentration procedure

Five milliliters solutions containing 0.4 μg ml^{-1} V(V) and V(IV) were prepared and the pH value was adjusted to 3.2 with 0.1 mol l^{-1} HCl and 0.1 mol l^{-1} NaAc. The solution was passed through the column by using a peristaltic pump at a desired flow rate. V(V) retained by the column was eluted with 300 μl of 0.5 mol l^{-1} HCl solution, while V(IV), which could not be retained and passed directly through the column, was collected and was adjusted to pH 6 with 0.1 mol l^{-1} NaOH, then was diluted to 6 ml. The resulting solution was subjected to the preconcentration of V(IV) by the column and the retained V(IV) was eluted with 300 μl of 0.5 mol l^{-1} HCl solution, too. The separated V species were determined by FETV–ICP-OES.

2.7.2. FETV–ICP-OES and FETV–ICP-MS procedure

It is well known that vanadium is a typical refractory element. When it was determined by ETV plasma spectrometry, an incomplete vaporization, much lower sensitivities and severe memory effects would be encountered. Our previous research [23] has been proved that PTFE emulsion was an effective fluorinating modifier for ETV–ICP-OES determination of refractory element V. In this work, FETV–ICP-OES and FETV–ICP-MS technique were both used to determination of vanadium, and the ETV parameters used in this study was the same as in reference [25]. After selecting analytical wavelength by pneumatic nebulization system, it was disconnected from the plasma torch, and replaced by the graphite furnace device. After plasma stabilizing, 10 μl prepared sample was pipetted into the graphite furnace with microsyringe, and the sample inlet hole was sealed with a graphite cylinder before the graphite furnace heating cycle was started. After drying and ashing, the analytes were vaporized and carried into the plasma by the argon gas under the optimized conditions. The peak heights were measured for quantification in FETV–ICP-OES, and the peak areas were measured for quantification in FETV–ICP-MS.

3. Results and discussion

3.1. Loading amount of quinine on resin and the stability of quinine modified resin

To evaluate the retention capacity of quinine on the weakly acidic cation exchange resin, the original solution of quinine as well as the resultant solution, which was collected after modifying the cation exchange resin together with the washing solution, was measured spectrophotometrically at quinine maximum absorbance of 250 nm. The loading amount of quinine on the weakly acidic cation exchange resin was calculated based on the difference between the concentration of quinine in above two solutions (before and after immobilizing) and was found to be 90.1 mg g^{-1}.

The stability of quinine modified resin was investigated by immersing the quinine modified resin in varying acidity medium. For this purpose, 100 mg of quinine modified resin were added into 0.1 ∼ 3.0 mol l^{-1} HCl, respectively, and the mixture was stirred ultrasonically for 30 min. After centrifugation, the concentration of quinine in the supernatant was determined spectrophotometrically at quinine maximum absorbance of 250 nm. The results showed that the percentage of quinine eluted in 0.1 ∼ 3.0 mol l^{-1} HCl were 0.97% ∼ 3.01%, indicating that the quinine modified resin possessed good stability.

3.2. Effect of pH

The pH value plays an important role with respect to the preconcentration and separation of V species. In order to evaluate the effect of pH, the pH values of sample solutions were adjusted to a range of 1 ∼ 7 with HCl or NaAc. The resin with/without quinine modification was employed to preconcentrate and separate V species with the sample volume and the sample flow rate fixing at 5 ml and 0.4 ml min^{-1}, respectively. Fig. 1 is the effect of pH on the recoveries of V(V) and V(IV) after subjected to the separation/preconcentration by the original resin and the quinine modified resin.

It is clear from Fig. 1A that both V(V) and V(IV) could not be adsorbed completely by the resin without quinine modification in the pH range of 1 ∼ 7. On the contrary, the quinine

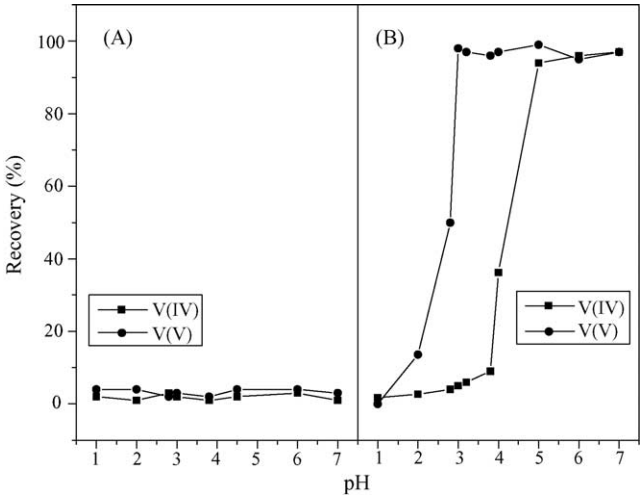

Fig. 1. Effects of pH on the recoveries of V(IV) and V(V) after separation/preconcentration by cation exchange resin and the quinine loaded resin. (A) weakly acidic cation exchange resin; (B) the quinine modified resin. V(IV), V(V): 0.4 μg ml^{-1}; sample flow rate: 0.4 ml min^{-1}.

modified resin showed different adsorption characteristics towards V(V) and V(IV) with pH ranging from 1 to 7 (Fig. 1B). At pH 3 ~ 7, V(V) could be adsorbed quantitatively by the quinine modified resin, and similarly, V(IV) could also be adsorbed quantitatively by the resin at pH 5 ~ 7. It also could be found from Fig. 1B that, at pH 3 ~ 3.8, V(V) can be selectively adsorbed quantitatively by the resin, while V(IV) could almost not be retained. This means that it is possible to separate V(V) and V(IV) with quinine modified resin by selecting the suitable pH. The possible reasons for these are that the quinine modified resin was a new kind of anion exchange resin, and V(IV) existed as stable cation of VO^{2+} under pH 3 ~ 3.8, and thus could not be adsorbed by the resin. However, for V(V), it mainly existed as the form of anion under the acidity condition, and could adsorbed by the resin at a broad pH range (pH 1 ~ 7) [27,28]. In the following experiments, pH 3.2 was selected for the separation of V(V) and V(IV). At this pH, V(V) could be quantitatively (~90%) retained by the quinine modified resin. The resulting solution of V(IV), which passed through the micro column, was subjected to the preconcentration of V(IV) after adjusting the pH to 6 with NaOH. Thus, V(V) and V(IV) could not only be separated basically but also get successively determined.

3.3. Effect of flow rates of sample solutions

As the retention of analytes on adsorbent depends upon the flow rate of the sample solution, the effect of sample flow rate was examined under the optimum pH (pH 3.2 for V(V) and pH 6 for V(IV), respectively) by passing 5 ml of sample solution through the micro-column with the flow rates varying in a range of 0.3 ~ 2.5 ml min^{-1}. The results indicated that quantitative recoveries of V(V) and V(IV) were obtained at the flow rates less than 0.5 ml min^{-1}. The recoveries of V(V) and V(IV) will decrease rapidly with increasing the flow rate from 0.5 to 2.5 ml min^{-1}, due to a decrease in the adsorption kinetics at a high flow rate. Thus, a flow rate of 0.4 ml min^{-1} is employed in this work.

3.4. Effect of desorption conditions

With respect to the stripping of V(V) and V(IV) from the quinine modified resin, HCl was employed and different concentration of HCl was studied for the elution of V(V) and V(IV) retained in the microcolumn at a flow rate of 1.0 ml min^{-1}. It was found when the concentration of HCl was in the range of 0.5 ~ 3.0 mol l^{-1}, V(V) and V(IV) were desorbed quantitatively and their recoveries remained constant (>90%). In addition, the effect of eluant volume of 0.5 mol l^{-1} HCl on the recovery of V(V) and V(IV) after retention was also investigated, and the results showed that quantitative recoveries could be obtained with 300 μl of 0.5 mol l^{-1} HCl.

The effect of desorption flow rate was examined at the eluent flow rate range of 0.3 ~ 2.5 ml min^{-1} with the eluant volume of 0.5 mol l^{-1} HCl fixed at 0.5 ml. The results were shown in Fig. 2. It was found that the recoveries of V(V) and V(IV) strongly depended on the eluent flow rate, the higher the flow rate of HCl, the lower recoveries of V(V) and V(IV). When the flow rate was controlled within 0.3 ~ 1.0 ml min^{-1}, the recoveries of V(V) and V(IV) were over 90%. Therefore, desorption flow rate of 1.0 ml min^{-1} was selected in this work.

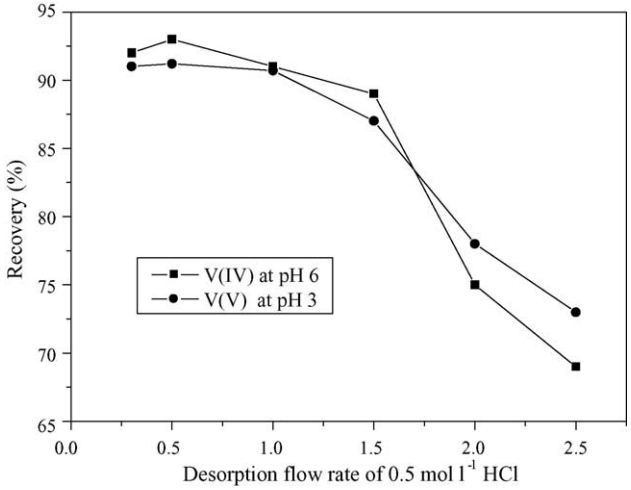

Fig. 2. Effect of desorption flow rate of 0.5 mol l^{-1} HCl on the recovery of V(IV) and V(V). V(IV), V(V):0.4 μg ml^{-1}.

3.5. Effect of ratio of V(IV) to V(V)

It has been predicated that the oxidation state of vanadium changes in aqueous solutions, and a standard solution of vanadium may contain mixtures of V(V) and V(IV) which change with time [29]. Nukatsuka et al. [10] and Okamura et al. [15] were also investigated the stability of V(V) and V(IV) in different kinds of water samples. The results showed that in artificial seawater at pH 7.8, V(V) was stable but V(IV) was oxidized rapidly, in acidified artificial seawater (pH 2.0), V(IV) was oxidized slowly but only a small tendency of such reduction of V(V) was observed, and in a natural seawater sample, V(IV) was not detected. The change in the redox equilibrium state may occur between V(V) and V(IV) in the air, and thus the contents of V species in aqueous solutions may be changed. Therefore, the effect of the ration of V(IV) to V(V) on the analytical results during the preconcentration and separation process has been evaluated. For this purpose, the pH and the concentration of V(V) were fixed at 3.2 and 0.4 μg ml^{-1} with the concentration of V(IV) changed as 0.8, 1.6, 2.4, 3.2 and 4.0 μg ml^{-1}, respectively (i.e. the ratio of V(IV) to V(V) are 2, 4, 6, 8 and 10). Then, the above sample solutions were passed through the micro-column under the optimal conditions. The results showed that the quantitative recovery of V(V) was obtained with ratio of V(IV) to V(V) ranging from 2 to 10, and this indicated that the species of V(V) and V(IV) were relatively stable under these conditions.

Table 2
Effect of sample volume on the recovery of V(IV) and V(V)

Sample volume (ml)	Concentration ($\mu g\,ml^{-1}$)		Recovery (%)	
	V(IV)	V(V)	V(IV)	V(V)
50	0.04	0.04	73.2	82.3
25	0.08	0.08	92.3	93.5
10	0.2	0.2	101.2	90.0
5	0.4	0.4	99.4	102.3

3.6. Effect of sample volume

Preconcentration and separation of vanadium were usually performed at lower concentration. To avoid inaccuracy when determining lower concentration of analyte, a relative large sample volume was usually suggested. For this purpose, 5, 10, 25 and 50 ml of sample volume were adopted to test the effect of sample volume. Mixed sample solutions containing 2 μg V(V) at pH 3.2 and 2 μg V(IV) at pH 6, were passed through the micro-column at the optimal flow rate and the results were listed in Table 2. It could be seen that the quantitative recoveries (over 90%) were obtained with sample volume less than 25 ml for V(V) and V(IV). As described previously, 300 μl of 0.5 mol l^{-1} HCl was enough to elute the analyte adsorbed in the micro column and the effluent was finally prepared into the volume of 400 μl slurry containing 6% (m/v) PTFE for FETV–ICP-OES analysis, the enrichment factor is about 62.5 with 25 ml of sample solution. Compared with the enrichment factor of 40 and 15 reported in literature [11] and [9], the enrichment factor of 62.5 obtained in this work is higher.

3.7. Adsorption capacity

The adsorption capacity is an important factor to evaluate the resin, because it determines how much quinine resin is required to quantitatively concentrate V(V) and V(IV) from a given solution. Under the optimal conditions, the determination of dynamic adsorption capacity was performed based on the procedure recommended by Maquieira et al. [30]. Ten milliliters aliquots of a series of concentrations ($1 \sim 20\,\mu g\,ml^{-1}$) was adjusted to the appropriate pH (pH 3.2 for V(V) and pH 6 for V(IV), respectively), then operated according to the general procedure described previously. A breakthrough curve was obtained by plotting the total V(V) and V(IV) concentration ($\mu g\,ml^{-1}$) versus the micrograms of V(V) and V(IV) adsorbed per gram, and the results are shown in Fig. 3. The adsorption capacity evaluated from the breakthrough curve is 7.6 and 8.0 mg g^{-1} for V(V) and V(IV), respectively.

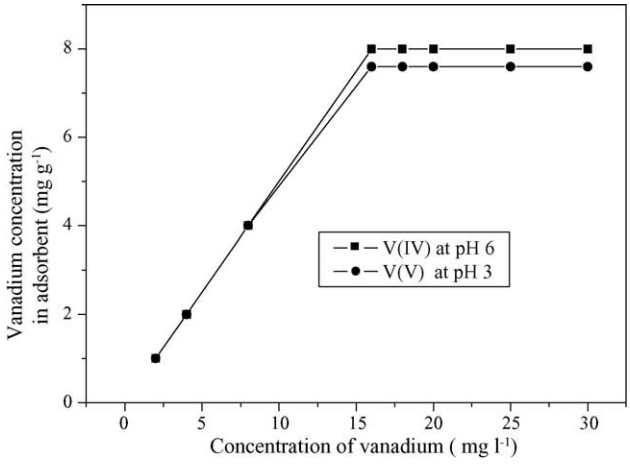

Fig. 3. The breakthrough curve of V(IV) and V(V) on the quinine modified resin.

3.8. Interference effects

The effects of common coexisting cations and anions on micro column separation/preconcentration of both vanadium species were examined. Solutions of 0.4 $\mu g\,ml^{-1}$ V(V) and V(IV) (pH 3.2 for V(V) and pH 6 for V(IV), respectively) containing the added interfering ions were treated according to the recommended procedure. The results indicated that 1000 $\mu g\,ml^{-1}$ Na^+, K^+, 500 $\mu g\,ml^{-1}$ Ca^{2+}, Mg^{2+}, 10 $\mu g\,ml^{-1}$ Cu^{2+}, Fe^{3+}, Ni^{2+}, 800 $\mu g\,ml^{-1}$ SO_4^{2-}, 1300 $\mu g\,ml^{-1}$ Cl^- and 2400 $\mu g\,ml^{-1}$ $H_2PO_4^-$ have no obvious influence on the separation and determination of V species under the selected conditions.

3.9. Detection limit and precision

With the use of established experimental parameters as shown in Table 1, the analytical performance of the method was evaluated. The limits of detection, defined as the analyte concentration that gives a signal that was three times the stan-

Table 3
Limits of detection (LOD) and precision (R.S.D.) of vanadium

R.S.D. (%)		Limit of detection (3σ) ($pg\,ml^{-1}$)		
FETV–ICP-OES	FETV–ICP-MS	FETV–ICP-OES	FETV–ICP-MS	Literature
4.9[a]	3.8[b]	72 (EF 62.5)	0.56 (EF 62.5)	19 (EF 15) [13][c]; 900 (EF 10) [9][d]

[a] 0.2 $\mu g\,ml^{-1}$, $n = 9$.
[b] 1.0 $ng\,ml^{-1}$, $n = 9$; EF, enrichment factor.
[c] By ICP-OES–USN.
[d] By FAAS.

Table 4
Analytical results of V(IV) and V(V) in water samples

Sample	Species	Added[a] (ng ml^{-1})	FETV–ICP-OES		FETV–ICP-MS	
			Found[b] (ng ml^{-1})	Recovery (%)	Found[b] (ng ml^{-1})	Recovery (%)
East Lake water	V(IV)	0	–	–	–	–
		5	5.20 ± 0.08	104	4.90 ± 0.18	98
		10	9.70 ± 0.12	97	10.60 ± 0.27	106
	V(V)	0	2.53 ± 0.09	–	2.79 ± 0.14	–
		5	7.90 ± 0.13	107	7.97 ± 0.22	103
		10	12.20 ± 0.23	96	13.70 ± 0.19	109
Tap water	V(IV)	0	–	–	–	–
		5	4.80 ± 0.15	98	5.10 ± 0.05	102
		10	10.30 ± 0.26	103	9.80 ± 0.09	98
	V(V)	0	1.87 ± 0.11	–	1.98 ± 0.05	–
		5	6.58 ± 0.14	94	7.10 ± 0.03	100
		10	12.30 ± 0.17	104	11.9 ± 0.08	99.2

–, Not detected.
[a] Added the same concentration of V(IV) and V(V).
[b] Mean ± average deviation, $n = 5$.

dard deviation of the blank with the preconcentration step in FETV–ICP-OES and FETV–ICP-MS techniques were calculated and the results are shown in Table 3. A comparison of detection limit obtained by different method for vanadium speciation is also made in Table 3. It can be seen that the limit of detection obtained by present method is lower than that obtained by reference [9] and a litter hit higher than reference [13].

3.10. Analytical application

3.10.1. Water sample analysis

The proposed method has been applied to the determination of V(V) and V(IV) in lake water and tap water (25 ml) and the analytical results obtained by FETV–ICP-OES together with FETV–ICP-MS are given in Table 4. As can be seen, the determined values obtained by both FETV–ICP-OES and FETV–ICP-MS coincided very well. The species of V in water are primarily V(V), and no V(IV) species could be detected. Table 4 also listed the recoveries for the spiked real water samples and fairly good recoveries for the two vanadium species were obtained.

Table 5
Analytical results of vanadium in GBW07401 soil and GBW07605 tea leaves reference materials by FETV–ICP-OES

Sample	Total V certified (μg g^{-1})	Found[a] (μg g^{-1})		
		Total V	V(IV)	V(V)
GBW07401 soil	86 ± 6	83.8 ± 6.4	–	83.8 ± 6.4
GBW07605 tea leaves	0.86[b]	0.77 ± 0.02	–	0.77 ± 0.02

–, Not detected.
[a] Mean ± average deviation, $n = 5$.
[b] Reference value.

3.10.2. Biological and environmental sample analysis

In order to verify the validity of the procedure, the method has been applied to the determination of the total content of V in biological and environmental standard reference materials (GBW07605 tea leaves and GBW07401 soil).

The separation and preconcentration of V in the above digested solutions and their determinations were performed according to the developed procedure, and the analytical results are given in Table 5. As can be seen, the species of V in the above digested solutions are primarily V(V), and the obtained results coincide very well with the certified values.

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