On-line separation/preconcentration of V(IV)/V(V) in environmental water samples with CTAB-modified alkyl silica microcolumn and their determination by inductively coupled plasma-optical emission spectrometry

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ABSTRACT

A simple and selective method of flow injection microcolumn separation/preconcentration on-line coupled with inductively coupled plasma-optical emission spectrometry (ICP-OES) was developed for the speciation of V(V)/(IV). Various factors affecting the separation/preconcentration of V(IV) and V(V) by conical microcolumn packed with cetyltrimethylammonium bromide (CTAB)-modified alkyl silica have been systematically investigated. It is found that V(V) was quantitatively retained by the microcolumn at pH 2.0–7.0, while V(IV) was not retained by the microcolumn at pH 2.0–3.5 but quantitatively retained at pH 5.0–7.0. The two vanadium species adsorbed by the modified adsorbent were quantitatively desorbed by 0.10 mL of 1.0 mol L^{-1} HNO$_3$. Therefore, V(V) and total vanadium could be determined by CTAB-modified alkyl silica packed microcolumn separation/preconcentration and on-line ICP-OES detection after adjusting sample solution to pH 2.5 and 6.0, respectively, and the assay of V(IV) was realized by subtracting V(V) from total V. The detection of limit (LOD) for V(V) was 0.03 μg L^{-1} with an enrichment factor of 27.9 for a 3.0 mL sample consumption. The relative standard deviations (RSDs) ($C_{V(V)} = C_{V(IV)} = 5.0$ μg L^{-1}, $n = 9$) were 4.3% and 4.0% for V(V) and total V, respectively. The developed method was validated by the determination of V(IV) and V(V) in environmental water samples.

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1. Introduction

As one of the major essential elements, vanadium is beneficial to normal cell growth. However, much higher content of vanadium shows toxic properties and its toxicity has been well documented [1]. With the increasing industrial activities, the content of vanadium in the environment is increasing very rapidly [2]. Under such circumstances, vanadium would enter and accumulate in human body through various ways, and natural water is one of the main routes [3]. In aqueous solution, V(IV) and V(V) are the most commonly existing forms and they exhibit different nutritional and toxic properties [1–3]. It has been approved that V(V) is largely responsible for the restraining effect to adenosine triphosphatase in the biological bodies, while V(IV) has little effect [4]. To investigate the different toxicities and essential nature of vanadium in biological systems, there has been more considerable interest in its speciation than total content measurement. Therefore, it is very important to develop accurate and reliable methods for the speciation of V(IV) and V(V) in environmental water samples.

Different analytical techniques have been used for trace vanadium analysis and its speciation in various samples, including spectrophotometry [5,6], atomic absorption spectrometry (AAS) [7–9], neutron activation analysis (NAA) [10], ICP-OES [4,11,12] and inductively coupled plasma mass spectrometry (ICP-MS) [13,14]. Among these techniques, ICP-OES/MS has become one of the powerful techniques for the determination of vanadium due to its attractive features including low detection limit, good precision, wide linear dynamic range, multi-element detection capacity, and high sample throughput.

However, owing to the extreme low concentration of vanadium (usually at the level of several μg L^{-1}) and severe matrix interference in real samples (such as seawater), an efficient separation/preconcentration step is often required prior to ICP-OES/MS determination. The separation techniques for the vanadium speciation could be generally classified into chromatographic techniques [13–15] and non-chromatographic techniques [3,4,7,10,11,16–25]. For a simple elemental speciation, especially for different oxidation states of a given element, non-chromatographic methods are more diffused than the chromatographic techniques. Among these non-chromatographic techniques, solid phase extraction (SPE) has been widely employed because it is convenient, low cost, easy-to-automate and time saving.

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Table 1
Operating parameters of Intrepid XP Radial ICP-OES.

RF generator power (W)	1200
Frequency of RF generator (MHz)	27.12
Plasma gas flow rate ($L min^{-1}$)	14
Carrier gas ($L min^{-1}$)	0.6
Auxiliary gas flow rate ($L min^{-1}$)	0.5
Integration times (s)	15
Analytical wavelength (nm)	309.311

It should be noted that the selection of adsorbents is one of the key factors in SPE and much attention has been paid to the investigation of new adsorption materials for SPE. Some solid phase adsorbents including chelating resin [7,21,24], multi-walled carbon nanotubes [8], ion-exchange resin [10], biosorbent material [11], functionalized cellulose adsorbent [18], and TTA modified-microcrystalline naphthalene [19] have been employed for the speciation of vanadium. However, due to the easy oxidation of V(IV) to V(V) by atmospheric oxygen at low acidity and similar chemical properties of the two oxidation states, it is difficult to directly separate V(IV) from V(V) in real samples by using a chelating reagent modified adsorbent [26]. In order to overcome this problem, 1,2-cyclohexanediaminetetraacetic acid (CDTA) was usually used as a masking agent for V(IV) [4,22], but the operation is laborious and it is associated with the possible contamination risk. Therefore, to explore new adsorbent with good selectivity, low cost and simple preparation for the separation of V(IV)/(V) arose extensive interest in analytical community [10].

In our previous work, an adsorbent of CTAB-modified alkyl silica was proposed for the speciation of inorganic As and Se in environmental water samples due to its good selectivity on anion-forming analytes [27]. In this work, the potential of the above mentioned adsorbent was explored, and a rapid and sensitive method for the speciation of vanadium (V/IV) by microcolumn separation/preconcentration combined with ICP-OES was developed. The retention and elution conditions for the separation and preconcentration of V(V) and V(IV) have been studied and the optimal experimental conditions were established. The developed method was applied to the determination of two vanadium species in environmental water samples with satisfactory results.

2. Experimental

2.1. Apparatus and operating conditions

Intrepid XP Radial ICP-OES (Thermo, Waltham, MA, USA) with a concentric nebulizer and a Cinnabar spray chamber was used for the determination of vanadium species. The instrument operating conditions and wavelength used are given in Table 1. The pH values were adjusted by a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A conical minicolumn (Φ 0.6 mm × 5 mm, 50 mm length, 200 μL pipet tip, Yuhua Experimental Instrument Factory, Haimen, Jiangsu, China) made of polypropylene material was used as the adsorbent holder. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) was employed in the optimization of sample pH, concentration of HNO_3, sample loading/elution flow rate, sample volume and adsorption capacity, followed by an off-line ICP-OES detection. An IFIS-C flow injection system (Ruimai Tech. Co. Ltd., Xi'an, China) was used for the elution volume optimization, analytical performance evaluation and real sample analysis, followed by an on-line ICP-OES detection.

2.2. Standard solutions and reagents

Stock solutions ($1.0 g L^{-1}$) of V(V) and V(IV) were prepared from analytical grade NH_4VO_3 (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and $VOSO_4 \cdot 5H_2O$ (Merck, Darmstadt, Germany), respectively, by dissolving their appropriate amounts in 100 mL of $0.01 mol L^{-1}$ HCl. Working standard solution were prepared fresh daily by stepwise dilution of the stock solution with high-purity deionized water (18.2 MΩ cm, Kansas, MO, USA) obtained from a Labconco system.

CTAB (+99%) was obtained from Acros Organics (New Jersey, USA). HCl and HNO_3 were of the highest purity available and obtained form Shanghai Reagent Co. Ltd. (Shanghai, China). $0.1 mol L^{-1}$ HAc–NaAc buffer was used to control pH values.

Alkyl silica (100–150 mesh) (The First Reagent Factory, Shanghai, China) was immersed in ethanol and $1 mol L^{-1}$ HNO_3 for 24 h sequentially. It was then filtered and washed with high-purity deionized water until neutral, and dried prior to storage for future use.

All laboratory ware made of polyethylene or polypropylene material were thoroughly cleaned by soaking in nitric acid (5%, v/v) for at least 24 h. Prior to use, all acid-washed containers were rinsed with high-purity deionized water.

2.3. Preparation of CTAB dynamically modified alkyl silica microcolumn

In this study, CTAB was dynamically coated on alkyl silica adsorbent, and the modification procedure was described in previous work [27]. Briefly, a total of 60 mg of alkyl silica material was filled into a 200 μL pipet tip plugged with a small portion of cotton at both ends. A pumping tube connected to the peristaltic pump or flow injection system was wound with enough polytetrafluoroethylene (PTFE) tapes and inserted tightly into the base end of the filled pipet tip, and the pointed end of the pipet tip was directly inserted into another pumping tube also connected to the peristaltic pump or flow injection system. One milliliter of 0.5% (m/v) CTAB was passed through the microcolumn at a flow rate of $0.5 mL min^{-1}$. After modification, 1 mL of $1 mol L^{-1}$ HNO_3 was passed through the microcolumn to elute the possible impurities. After cleaning with 2 mL of high-purity deionized water, the microcolumn was conditioned to the desired pH with appropriate HAc–NaAc buffer solution. The modification procedure was repeated after every 15 times usage of the column.

2.4. General procedure

Certain volume of aliquots of sample solution containing the analytes of interest was divided into two parts, which were named samples 1 and 2 and their pH values were adjusted to pH 2.5 and 6.0, respectively. The operation sequence of the FI on-line microcolumn preconcentration and determination is shown in Fig. 1. In preconcentration step, pump P1 was activated. Three milliliters of sample 1 was pumped through the microcolumn at a flow rate of $1.7 mL min^{-1}$, and then high-purity deionized water was passed through to wash off the residual sample matrix on the column. After that, pump P2 was activated in elution step, in which the retained V(V) was eluted with 0.10 mL of $1.0 mol L^{-1}$ HNO_3 at a flow rate of $1.7 mL min^{-1}$, and the eluent was directly introduced into ICP-OES for V(V) determination. Similarly, 3 mL of sample 2 was processed using the same procedure mentioned above and the concentration of total V was determined. The concentration of V(IV) in the sample solution was calculated by subtracting V(V) from total V.

Two replicates of high-purity deionized water were used as the blank solutions. The blank values for V(V) and total V were determined after the blank solutions were subjected to the same
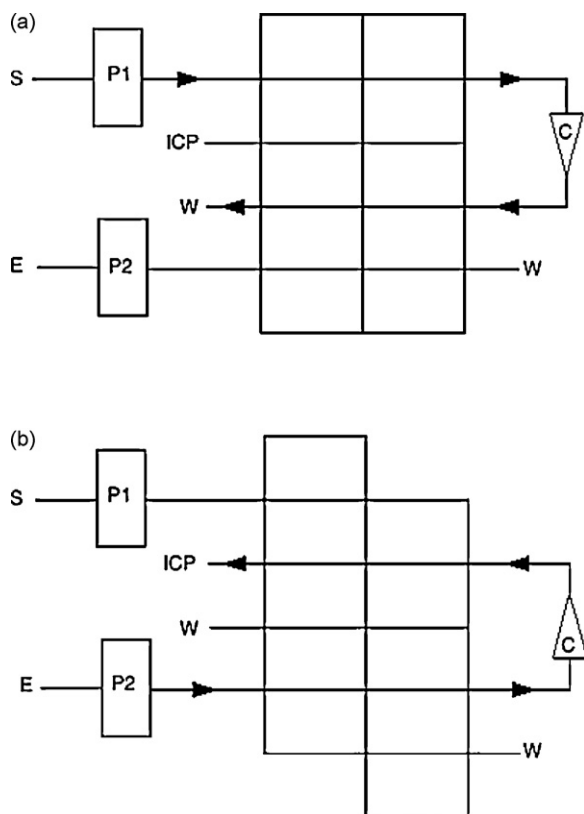
Fig. 1. FI manifold and operation for on-line preconcentration/separation and ICP-OES determination. (a) Preconcentration/separation step; (b) elution/introduction step. For details see text. S, sample; E, elution; W, waste; C, conical minicolumn packed with CTAB-modified alkyl silica; P1, P2, peristaltic pumps; ICP, ICP torch.

procedures as that for samples 1 and 2. The actual concentrations of the species were obtained after blank subtraction.

The quantitative analysis was performed by the external standard method: the calibration curve was obtained after subjecting a series of standard solutions (0.1, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0, 500.0 μg L^{-1}) to the same analytical procedure. The calibration curve was obtained, and the concentrations of analytes in the samples were calculated based on the calibration curve.

2.5. Sample preparation

Three surface seawater samples and ten fresh water samples were collected and filtered through 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China) made of polytetrafluoroethylene material. After filtration, each of filtrates was immediately subjected to the analytical procedure described above to avoid the possible transformation of V species.

3. Results and discussion

3.1. Optimization of CTAB concentration

Fixing the volume and flow rate of CTAB at 1.0 mL and 0.5 mL min^{-1}, respectively, the optimum concentration of CTAB loaded onto alkyl silica was estimated. It is found that the adsorption percentage of V(V) at pH 2.5 was higher than 90% when the concentration of CTAB was higher than 0.05% (m/v). Similar results were also obtained for V(IV) at pH 6.0. Considering the possible competitive adsorption of other ions, a higher concentration of 0.5% (m/v) was used in future work.
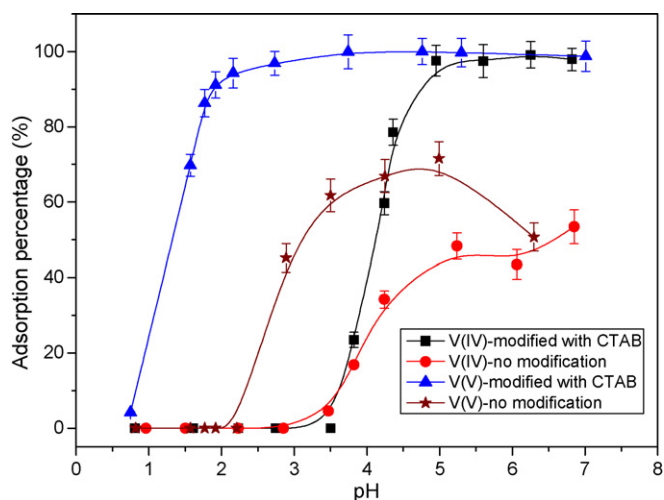

Fig. 2. Effect of pH on the adsorption percentage of vanadium species on the adsorbent with/without CTAB modification. Conditions: V(IV/V), 1.0 mg L^{-1}; sample volume, 3.0 mL; eluent, 1.0 mol L^{-1} HNO$_3$; eluent volume, 0.10 mL; sample loading/eluting flow rate, 1.7 mL min^{-1}.

3.2. Effect of pH

The pH of solution plays an important role in the separation/preconcentration of vanadium species. The effect of the acidity of the aqueous solutions on the adsorption of 1.0 mg L^{-1} V(IV) and 1.0 mg L^{-1} V(V) in the microcolumn of alkyl silica material with or without CTAB modification was examined in a pH range of 1.0–7.0. As can be seen in Fig. 2, quantitative adsorption could not be obtained for either of V species on the untreated silica adsorbent in the studied pH range, while the CTAB-modified alkyl silica material showed different adsorption characteristics towards V(V) and V(IV) in the pH range of 1.0–7.0. V(V) was quantitatively adsorbed by the CTAB-modified silica adsorbent in the pH range of 2.0–7.0, while V(IV) was not retained by the microcolumn at pH 2.0–3.5 but quantitatively adsorbed at pH 5.0–7.0. This means that by selecting a proper pH (pH range of 2.0–3.0), V(V) and V(IV) could be separated by microcolumn packed with CTAB-modified adsorbent. The possible reason for this could be attributed to the cationic surfactant characteristics of CTAB and the existing charged forms of V(IV) and V(V) at different pH. CTAB is a cationic surfactant, therefore, CTAB-modified alkyl silica material could be behaved as an anion exchange adsorbent to selectively adsorb negatively charged ions. V(IV) existed as a cation (VO^{2+}) at high acidity (pH < 3.5), and thus was not adsorbed in the pH range of 1.0–3.5. While V(V) mainly existed in anionic form when pH was higher than 2.0, and thus was quantitatively adsorbed by the adsorbent in the pH range of 2.0–7.0 [4,5]. In the subsequent experiments, pH 2.5 was selected for the assay of V(V) and pH 6.0 was employed for the assay of total V. V(IV) concentration was calculated by subtracting V(V) from total V.

Okamura et al. [21] have studied the redox behavior of V(V) and V(IV) in Millipore Milli-Q Water (MQW). It was found that V(V) was stable in a wide pH range, by contrast, V(IV) was stable only at pH 2.0 and gradually oxidized at pH 5.6. Similar results were also obtained by Filik et al. [4]. Therefore, the operation of real sample analysis was immediately performed after pH adjustment to avoid possible oxidation of V(IV) to V(V).

3.3. Effect of sample flow rate

The sample flow rate should be optimized to ensure quantitative adsorption of the target species. The influences of the sample flow rate on the adsorption percentage of 1.0 mg L^{-1} V(V) (pH 2.5) and 1.0 mg L^{-1} V(IV) (pH 6.0) were studied and the results

Table 2
Comparison of the adsorption capacity of V(IV) and V(V) on different adsorbents.

Adsorbent	Adsorption capacity		Operation mode	Literature
	V(V)	V(IV)		
CTAB-modified alkyl silica material	20.7 mg g^{-1}	12.8 mg g^{-1}	Column	This work
Amberlite XAD-P.Ox resin	46 μmol g^{-1}	40 μmol g^{-1}	Batch	4
TCPP-modified amberlite IRA-904 resin	47.5 μg g^{-1}	–	Column	7
Quinine modified resin	7.6 mg g^{-1}	8.0 mg g^{-1}	Column	10
TTA immobilized on microcrystalline naphthalene	1.20 mg g^{-1}	1.07 mg g^{-1}	Column	19
Imidazole 4,5-dicarboxylic acid resin	1.57 mmol g^{-1}	0.45 mmol g^{-1}	Batch	20

(–) not reported; P.Ox: palmitoyl quinolin-8-ol; TCPP: tetrakis (*p*-carboxyphenyl) porphyrin; TTA: thenoyltrifluoroacetone.

demonstrated that quantitative recoveries could be obtained for both species when the sample flow rate was varied from 0.4 to 1.7 mL min^{-1}, indicating a rapid reaction mechanism between V(V)/(VI) and CTAB-modified adsorbent at appropriate pH values. In the subsequent experiments, a sample flow rate of 1.7 mL min^{-1} was used.

3.4. Optimization of elution conditions

3.4.1. Concentration of HNO$_3$

As could be seen in Fig. 2, neither of V species was adsorbed by the CTAB-modified adsorbent in high acidity medium because V(IV) and V(V) existed in cationic forms and CTAB-modified silica adsorbent behaved as an anion exchange adsorbent. Therefore, in this work, HNO$_3$ was used as an eluent to elute the V species adsorbed on the CTAB-modified silica adsorbent. The influences of HNO$_3$ concentration on the recovery of 1.0 mg L^{-1} V(V) (pH 2.5) and 1.0 mg L^{-1} V(IV) (pH 6.0) from the microcolumn were studied by keeping the eluent volume equal to the sample volume (1.0 mL) and the eluent flow rate at 1.7 mL min^{-1}. The results indicated that both V(IV) and V(V) were quantitatively recovered when the concentration of HNO$_3$ was varied from 0.25 to 3.0 mol L^{-1}. In this work, 1.0 mol L^{-1} HNO$_3$ was used for the quantitative recovery of V(V) and total V.

3.4.2. Eluent flow rate

The influences of the eluent flow rate on the recovery of 1.0 mg L^{-1} V(V) (pH 2.5) and 1.0 mg L^{-1} V(IV) (pH 6.0) were studied by keeping the eluent volume and eluent concentration at 1.0 mL and 1.0 mol L^{-1}, respectively. The results showed that no obvious effect of the eluent flow rate on the recovery was observed in tested flow rate range of 0.4–1.7 mL min^{-1}. In the subsequent study, the eluent flow rate was set at 1.7 mL min^{-1} in order to shorten the analysis time.

3.4.3. Eluent volume

An eluent volume as low as possible is preferred for a high enrichment factor. Therefore, three respective portions (0.10 mL each) of the eluent were passed through the microcolumn continuously at 1.7 mL min^{-1} and the concentrations of the species in each portion were determined by on-line ICP-OES. The results indicated that quantitative recoveries of 1.0 mg L^{-1} V(V) (pH 2.5) and 1.0 mg L^{-1} V(V) (pH 6.0) were obtained within the first 0.10 mL of eluent. Therefore, 0.10 mL of 1.0 mol L^{-1} HNO$_3$ was used as the eluent in the subsequent experiments.

3.5. Sample volume

The effect of sample volume on the recovery of V(V) and V(IV) was studied by passing different volumes (2.0–50.0 mL) of two standard solutions through the microcolumn. The absolute amounts of the V(V) and V(IV) species were both 0.50 μg, and the pH of the solutions for V(V) and V(IV) was 2.5 and 6.0, respec-

tively. The results indicated that the recoveries of vanadium species were always above 90% and remained constant in the whole studied range. As described in the previous section, both V(V) and V(IV) were quantitatively recovered using a volume of 0.10 mL of 1.0 mol L^{-1} HNO$_3$, therefore, a theoretical enrichment factor of 500 for both V(V) and V(IV) could be obtained with a consumption of 50.0 mL sample solution. To trade off the enrichment factor and analytical speed, sample volume of 3.0 mL was used in real sample analysis.

3.6. Adsorption capacity

The adsorption capacity of CTAB-modified alkyl silica material was obtained by using breakthrough curve. Under the optimal conditions, 200 mL sample solution containing 10.0 mg L^{-1} V(V) (pH 2.5) and V(IV) (pH 6.0) was passed through the column continuously, 40 equal portions (each in 5 mL) were collected and the analyte concentration in every portion was determined by ICP-OES, respectively. Based on the method recommended in literature [28], the adsorption capacity evaluated from the breakthrough curve was 20.7 mg g^{-1} for V(V) at pH 2.5 and 12.8 mg g^{-1} for V(VI) at pH 6.0, respectively. Compared to the other adsorbents reported in literatures as shown in Table 2, the adsorption capacity of CTAB-modified alkyl silica material for vanadium species were far higher than those reported in literatures [4,7,10,19], while lower than those reported in literature [20].

3.7. Coexisting ions interference

Various coexisting ions were added individually to solutions containing 0.050 mg L^{-1} V(V) (pH 2.5) and V(IV) (pH 6.0), respectively, and their effects on the recovery of V(V) and V(IV) were investigated. The tolerance limits of coexisting ions, which gave less than 5.0% error for the determination of V(V) and V(VI), were evaluated, and results were listed in Table 3. As can be seen, the presence of major cations and anions had no obvious influence on the determination of V(V) and V(IV) under the selected conditions.

Table 3
Tolerance concentrations of coexisting ions.[a]

Ions	Tolerance limit (mg L^{-1})
K$^+$, Na$^+$	10,000
Ca^{2+}, Mg^{2+}	2000
Ba^{2+}	1000
Fe^{3+}, Zn^{2+}, Cu^{2+}	500
Co^{2+}, Mn^{2+}	100
Al^{3+}	50
Ni^{2+}	5
CH$_3$COO$^-$, H$_2$PO$_4$$^-$	10,000
Cl$^-$	30,000
SO$_4$$^{2-}$	8000
Citrate$^-$	2000

[a] Concentration of V(VI) and V(V), 0.050 mg L^{-1}; sample volume, 3.0 mL; eluent, 1.0 mol L^{-1} HNO$_3$; eluent volume, 0.10 mL; sample loading/eluting flow rate, 1.7 mL min^{-1}.

Table 4
Recovery values of V(V) and total V determined at different concentration ratios of V(V) and V(IV), as well as the calculated V(IV) concentrations (mean ± SD, $n = 3$).[a]

V(V)/V(IV)	V(V)			V (total)		V(IV)
	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)	Calculated ($\mu g\,L^{-1}$)
0.05	10.0	11.2 ± 0.19	112	197.5 ± 6.71	94	186.3 ± 6.51
0.1	10.0	9.5 ± 0.15	95	100.1 ± 2.70	91	90.6 ± 2.55
1	10.0	9.0 ± 0.12	90	19.9 ± 0.41	99	10.9 ± 0.29
10	10.0	10.1 ± 0.31	101	11.0 ± 0.47	100	0.9 ± 0.12
20	10.0	9.8 ± 0.24	98	10.4 ± 0.25	99	0.6 ± 0.02

[a] Sample volume, 3.0 mL; eluent, 1.0 mol L^{-1} HNO$_3$; eluent volume, 0.10 mL; sample loading/eluting flow rate, 1.7 mL min^{-1}.

Table 5
Speciation of vanadium in environmental reference material (mean ± SD, $n = 3$).[a]

Certified value (mg L^{-1})	Determined values (mg L^{-1})		
Total V	Total V	V(V)	Calculated V(IV)
Reference water sample (GSBZ 50029-94 (03502)) 0.500 ± 0.022	0.514 ± 0.040	0.468 ± 0.019	0.046 ± 0.005

[a] Sample volume, 3.0 mL; eluent, 1.0 mol L^{-1} HNO$_3$; eluent volume, 0.10 mL; sample loading/eluting flow rate, 1.7 mL min^{-1}.

Table 6
Speciation of vanadium in environmental water samples (mean ± SD, $n = 3$).[a]

Sample	Added V		V(V)		V(total)		Calculated V(IV) ($\mu g\,L^{-1}$)
	V(IV)	V(V)	Found ($\mu g\,L^{-1}$)	Recovery (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)	
Seawater 1[b]	0	0	0.9 ± 0.12	–	1.4 ± 0.17	–	0.5 ± 0.05
	2.0	8.0	3.1 ± 0.34	108	10.3 ± 0.35	90	7.2 ± 0.10
Seawater 2[c]	0	0	1.8 ± 0.12	–	3.4 ± 0.35	–	1.6 ± 0.23
	2.0	8.0	3.6 ± 0.21	95	11.5 ± 0.42	86	7.9 ± 0.21
Seawater 3[d]	0	0	0.5 ± 0.05	–	1.3 ± 0.15	–	0.8 ± 0.10
	2.0	8.0	3.0 ± 0.15	120	11.3 ± 0.86	100	8.3 ± 0.71
Yangtze river water[e]	0	0	1.0 ± 0.10	–	2.2 ± 0.17	–	1.2 ± 0.07
	2.0	8.0	3.1 ± 0.10	103	12.1 ± 0.93	99	9.0 ± 0.80
East lake water 1[f]	0	0	1.3 ± 0.05	–	4.7 ± 0.42	–	3.4 ± 0.37
	4.0	4.0	4.6 ± 0.40	87	14.6 ± 0.50	115	10.0 ± 0.12
East lake water 2[g]	0	0	1.2 ± 0.21	–	3.0 ± 0.35	–	1.7 ± 0.14
	4.0	4.0	4.5 ± 0.15	87	11.1 ± 1.41	101	6.7 ± 1.26
Well water[h]	0	0	4.2 ± 0.42	–	16.0 ± 1.48	–	11.7 ± 1.06
	4.0	4.0	8.3 ± 0.21	101	23.3 ± 0.70	97	15.1 ± 0.49
Ancient well water[i]	0	0	1.4 ± 0.20	–	1.7 ± 0.06	–	0.4 ± 0.04
	4.0	4.0	5.0 ± 0.35	93	8.7 ± 0.49	90	3.8 ± 0.14
Rain water 1[j]	0	0	1.5 ± 0.14	–	2.3 ± 0.14	–	0.8 ± 0.01
	4.0	4.0	5.0 ± 0.56	91	9.4 ± 0.49	91	4.4 ± 0.07
Rain water 2[k]	0	0	1.6 ± 0.14	–	1.8 ± 0.07	–	0.2 ± 0.02
	4.0	4.0	5.3 ± 0.70	95	9.8 ± 0.77	100	4.5 ± 0.07
Pool water[l]	0	0	1.2 ± 0.07	–	2.1 ± 0.14	–	0.9 ± 0.07
	4.0	4.0	4.7 ± 0.28	90	9.8 ± 0.14	97	5.1 ± 0.14
Tap water[m]	0	0	1.7 ± 0.14	–	2.4 ± 0.42	–	0.7 ± 0.08
	4.0	4.0	6.7 ± 0.35	117	10.3 ± 0.28	99	3.6 ± 0.07

[a] Sample volume, 3.0 mL; eluent, 1.0 mol L^{-1} HNO$_3$; eluent volume, 0.10 mL; sample loading/eluting flow rate, 1.7 mL min^{-1}.
[b] pH 7.8, Xiaomeisha, Shenzhen, Guangzhou, China.
[c] pH 7.6, Gold Shore, Quanzhou, Fujian, China.
[d] pH 7.5, Xinghaiwan, Dalian, Liaoning, China.
[e] pH 7.5, Wuhan, Hubei, China.
[f] pH 7.7, below 1 m of the surface.
[g] pH 7.8, surface water.
[h] pH 7.1, Yiling, Yichang, Hubei, China.
[i] pH 6.2, Zhuodaoquan Temple, Wuhan, Hubei, China.
[j] pH 5.6, collected at the beginning of the raining season in Wuhan, China.
[k] pH 5.5, collected at the middle of the raining season in Wuhan, China.
[l] pH 7.3, Weiming Pool, Wuhan University, Hubei, China.
[m] pH 7.3, the tap in the laboratory.

It seems that the CTAB-modified alkyl silica material had a good selectivity for the speciation analysis of V(IV) and V(V). Since the presence of large numbers of alkali and alkaline-earth metals had no obvious effect on the recovery of V(V) and V(VI), the proposed method could be used for the speciation of V(IV)/(V) in seawater samples, in which alkali metals (such as Na^+) and alkaline-earth metals (such as Mg^{2+}) exist at gL^{-1} levels.

3.8. Sample throughput

The overall time required for the pretreatment of 3.0 mL sample solution was about 2.5 min, including loading (106 s), washing (15 s), eluting (4 s for 0.10 mL eluent), conditioning (20 s) at a flow rate of 1.7 mL min^{-1} and valve transfer (5 s). Therefore, the sample throughput was about 24 samples per hour.

3.9. Analytical performance

The analytical performance of the method was evaluated. A good linear relationship was obtained over the vanadium concentration range of 0.1–500.0 μg L^{-1} with a correlation coefficient of 0.9992. The limit of detection (LOD) for V(V) (3σ) was 0.03 μg L^{-1} using a sample volume of 3.0 mL. Better LODs can be achieved with much larger sample volume, whereas the analytical time would be prolonged. The relative standard deviations (RSDs) for 9 replicate determinations at 5.0 μg L^{-1} level of vanadium species were 4.3% for V(V) at pH 2.5 and 4.0% for total V at pH 6.0. The enrichment factor of this method was 27.9 for V(V) which was calculated by comparing the slope of the calibration graph of the developed method (287.4) with the slope of the calibration graph obtained directly by ICP-OES (10.3, without preconcentration).

3.10. Regeneration

The regeneration is one of the key factors for evaluating the performance of the adsorbent. Under the optimal conditions, a column packed with CTAB-modified alkyl silica adsorbent (dynamically modification) was subjected to the proposed procedure in a consecutive manner and it is found that the column could be re-used at least 15 times.

3.11. Effect of V(IV)/V(V) ratio

The shifting of the redox equilibrium between V(V) and V(IV) may occur in the air, and thus the contents of species in aqueous solutions may be changed [4,21]. Therefore, the effect of V(IV)/V(V) ratio on the analytical results during the separation and preconcentration process has been evaluated. Various synthetic samples with different V(IV)/V(V) concentration ratios were used and the results are given in Table 4. The two species of vanadium were completely separated and recovered quantitatively with V(IV)/V(V) ratio varying from 0.05 to 20.

3.12. Sample analysis

In order to validate the proposed method, a certified reference material of GSBZ 50029-94 (03502) environmental water (Institute of Reference Materials, SEPA Beijing, P.R. China) was analyzed, and the analytical results are given in Table 5. As can be seen, almost no V(IV) was found in the reference water sample, likely because the reference water sample has been stabilized at low acidity for a long time, leading to the oxidation of V(VI) to V(V). The determined values of V(V) and total V agreed well with the certified total V value.

The method was also successfully applied to the speciation of V(V)/V(IV) in environmental water samples including three surface seawater samples and ten fresh water samples. As can be seen in Table 6, the concentrations of V(V) and V(IV) in environmental water samples were in the range of 0.5–4.2 and 0.2–11.7 μg L^{-1}, respectively. In these seawater samples, concentrations of V(V) and V(IV) were similar to those reported in literature [4,24], but a little higher concentrations of V(V) were found in the present study respect to those reported in literature [21], probably because of the different geographical area. For rain water analysis, both species of V(IV) and V(V) were found and their concentrations were a little higher than those reported in literature [21]. For other samples (include river water, lake water), the concentrations of V(V/IV) obtained were a little higher than those reported in literature [21,22]. Additionally, in this study, both vanadium species were found in fresh environmental water samples, and similar results were reported in some literatures [3,22]. But only V(V) was found in some environmental water samples as reported in some other literatures [10,12,19].

4. Conclusion

In the present paper, a novel method of CTAB-modified alkyl silica packed microcolumn on-line coupled with ICP-OES has been proposed for the speciation of V(IV)/V(V) in environmental water samples. The speciation scheme is based on electrostatic action between the CTAB-modified material and the retained V species. No chelating reagent was used in this experiment, avoiding the possible contamination risks. The proposed method was simple, fast, and selective, and it could be adapted for rugged and routine use by the contract lab population and practitioners in water field who utilize such analyses.

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