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Vanadium speciation by ion chromatography

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Abstract. An ion-chromatographic method, using a carbonate-buffered (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) eluant, is described for the simultaneous determination of vanadium(IV) and vanadium(V). Vanadium(IV) was, after pre-column complexation with CDTA, separated from vanadium(V) (as vanadate) by anion-exchange chromatography. The analytical range is 0.5 to 20 μg/ml and 0.25 to 10 μg/ml for vanadium(IV) and vanadium(V), respectively. Detection limits are estimated to be 145 and 70 ng/ml for vanadium(IV) and vanadium(V), respectively.

1 Introduction

Until recently, the chemical speciation of metals has mainly been directed towards the interpretation of their roles in environmental and biological studies [1, 2]. Interest has now extended to establishing the importance of the speciation for a better understanding of industrial processes.

The importance of the simultaneous determination of vanadium in its different oxidation states is reflected in the growing number of publications dealing with the matter [3–9]. This can be contributed to a number of reasons:

Environmental. Vanadium is emitted into the environment from vanadium refineries, iron and steel industries, and chemical industries. Among the latter are the phosphate industries, which are a major source of vanadium pollution [10]. Due to the increase in production by these industries, there has been concern about increases in the environmental levels of vanadium – a phenomenon that needs to be monitored closely.

Biological. Vanadium is an essential trace element, possessing specific physiological functions. However, numerous reports have warned of the carcinogenic and other toxic effects of vanadium, resulting from excessive industrial exposure [10]. Studies have shown that vanadium, when administered as vanadate (vanadium(V)), is physiologically more active in fish, than are other species of vanadium [11].

Industrial. Vanadium metal is present in alloys and other industrially important materials. It can be used as a catalyst in numerous industrial processes, e.g. the Stretford, Unisulf, Shafer, and Sulfolin processes [12]. In these processes (and in alloys) vanadium is capable of existing simultaneously in its different valence states. For a thorough understanding of the chemistry involved in these processes, the determination of vanadium in its different oxidation states is essential.

Although there are many methods available for the determination of vanadium, hardly any can simultaneously separate and quantitatively determine vanadium(IV) and vanadium(V).

Spectrophotometry [3, 4, 13], flow-injection analysis (FIA) [14], chromatography [3, 8], neutron activation [3, 15], atomic-absorption spectroscopy (AAS) [3, 16, 17] and inductively coupled plasma atomic-emission spectroscopy (ICP-AES) [18–20] are but some of the techniques used for vanadium determination, most of which can determine only one oxidation state at a time. Determination of the total vanadium frequently requires the conversion of all the oxidation states to a single state. This step becomes very troublesome in complex sample matrices.

A method for the fractional determination of nanogram amounts of vanadium(IV) and vanadium(V) in natural waters has been developed by Nakano and coworkers [6]. The method is based on the solvent extraction of these ions into toluene at different pH-values with N-cinnamoyl-N-(2,3-xylyl)hydroxylamine.

Komarova and co-workers [8] proposed the anion-chromatographic separation of the vanadium(IV)- and vanadium(V)-ethylenediaminetetra-acetic acid (EDTA) complexes, with subsequent conductometric detection. Unfortunately, no baseline resolution of the vanadium(IV) and vanadium(V) peaks was achieved. A further disadvantage of this method is the use of conductivity as the detection mode, since it is almost impossible to detect the vanadium species in complex inorganic sample matrices in this way. The method has therefore only limited application.

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Hirayama and co-workers [21] suggested a two-column liquid-chromatography system. Under suitable conditions, each species was adsorbed onto a differently prepared column, from which they were separately eluted and detected by ICP-AES. Due to the selectivity of the detection mode, no significant interferences were observed. The technique does, however, require a considerable time for each analysis.

In this paper, an ion-chromatographic method for the separation and photometric detection of vanadium(IV) and vanadium(V) is described. Vanadium(IV) forms a strong complex with (1,2-cyclohexylene-dinitrilo)tetraacetic acid (CDTA), and can be separated from vanadium(V) by anion exchange, using an appropriate carbonate-bicarbonate-CDTA eluant. On-line detection of the species was done photometrically at 282 nm. The method was applied to various samples and proved to be simple, rapid, and accurate.

2 Experimental

The liquid chromatograph consisted of a Dionex 2000i Ion Chromatograph, a Linear UVIS 200 variable-wavelength photometric detector, and a Spectra-Physics SP 4270 integrator. The experimental conditions are summarized in Table 1.

A stock solution of eluant was prepared by dissolving 2.352 g of $NaHCO_3$, 2.438 g of Na_2CO_3, and 36.436 g of Titriplex IV (CDTA) in 1000 ml of water. The CDTA was predissolved in water to which NaOH pellets (8 to 10) were added. A five-times dilution of the eluant stock solution was made for chromatographic purposes.

Stock solution of vanadium(IV) and vanadium(V) were prepared as follows:

2 g/l vanadium(V): 4.58 g of NH_4VO_3 was dissolved in 1000 ml water.

2 g/l vanadium(IV): 4.96 g $VOSO_4 \cdot 5H_2O$ was dissolved in 250 ml of a 100 mmol/l CDTA solution, and diluted to 500 ml.

Standards were prepared by appropriate dilutions of the stock solution. Samples were prepared in a 10% solution of eluant stock. All the chemicals were of analytical-grade purity (Merck), and distilled water was used throughout.

Table 1. Experimental conditions

Column	Dionex, IONPAC AG5 GUARD	
Sample loop	50 µl	
Eluant	5.6 mmol/l $NaHCO_3$, 4.6 mmol/l Na_2CO_3, 20 mmol/l CDTA	
Eluant flow rate	$\mu = 0.5$ ml/min	
Detection: λ	282 nm	766 nm
range	0.1 abs	0.01 abs
output attenuation	128	64

3 Results and discussion

3.1 V(IV) stability

Solutions of vanadium(IV) with pH-values less than 2.45 and at 14 °C are stable for weeks [22], while the rate of oxidation increases rapidly at higher pH-values. Dean and Herringshaw [23] investigated the air-oxidation of vanadium(IV) in neutral and alkaline solutions. They found that oxidation proceeds rapidly at temperatures higher than 14 °C via the reduction of oxygen to peroxide:

$$O_2 + 2VO_3^{2-} + 2H_2O \rightarrow 2VO_3^- + 2OH^- + H_2O_2$$

$$H_2O_2 + 2VO_3^{2-} \rightarrow 2VO_3^- + 2OH^-$$

When the vanadium concentrations are greater than 0.1 g/l, the rate of oxidation is controlled by the diffusion rate of aerial oxygen. Analysis of alkaline vanadium solutions must therefore incorporate the stabilization of vanadium(IV).

CDTA has previously been used for the selective determination of vanadium(V) with 4-(2-pyridylazo)-resorcinol (PAR), since it forms strong complexes with most of the other transition metals, including vanadium(IV) [24]. In order to test the stability of the vanadium(IV)-CDTA complex, vanadium(IV) standards were prepared in CDTA. These standards were frequently tested for traces of vanadium(V) over a period of four weeks. This was done chromatographically with a PAR post-column reactor, since vanadium(V) reacts with PAR to form a very sensitive complex that absorbs at 540 nm. No traces of vanadium(V) were observed.

In neutral to alkaline solutions, vanadium(V) exists as the vanadate anion. Depending on the pH-value of the solution, it can be present as $H_2VO_4^-$ (pH 4 to 8), HVO_4^{2-} (pH 8 to 13) or VO_4^{3-} (pH 13 to 14) [25].

From the absorption spectra of vanadium(IV) and vanadium(V) in an aqueous CDTA solution (Fig. 1) and from investigations by Root [26], it is clear that both vanadium(IV)-CDTA and vanadate have photometric absorption maxima around 270 nm. It should therefore be possible to detect the two species if they could be separated by anion exchange. Since vanadium(IV)-CDTA is the less sensitive species of the two, 282 nm, which is the wavelength of maximum absorption of this complex, was chosen for the investigation. Vanadium(V) absorbs strongly at 282 nm, even though it has an absorption maximum at 294 nm.

3.2 Column and eluant choice

A carbonate-bicarbonate buffer, similar to that used for standard anion separation, was tested as eluant, using an IONPAC AS5 separating column. The vanadium(IV)-CDTA complex eluted from the column with reasonable ease, but no vanadium(V) could be detected. In an attempt to elute the vanadium(V) from the column, CDTA was added to the eluant. Theoretically, the CDTA should compete with vanadium(V) for the exchange sites on the column, and thus permit faster elution of the vanadium(V). This was indeed observed, since both

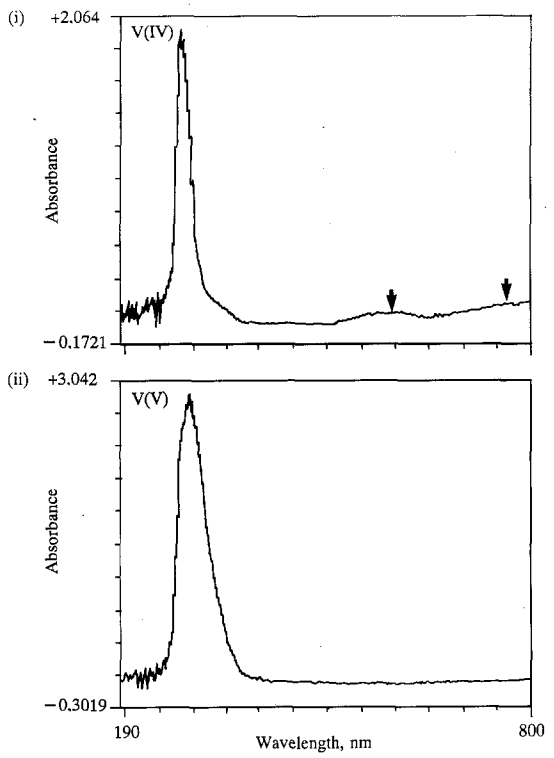

Fig. 1. Absorption spectra for (*I*) V(IV)-CDTA; (*II*) V(V) (Similar, in water and CDTA)

vanadium(IV) and vanadium(V) could now be detected. Respective retention times of approximately six and seventeen minutes were observed. A considerable degree of vanadium(V) peak-broadening did unfortunately occur.

An IONPAC AG5 guard column, which has the same characteristics as the IONPAC AS5, but is shorter, was tested using otherwise identical conditions. Very good separations and sharper peaks were achieved. In order to achieve complete separation of the vanadium(IV) peak and the solvent front, the eluant flow rate was reduced from 1 to 0.5 ml/min. A chromatogram for this separation is shown in Fig. 2.

Chromatograms of the two vanadium species, using varying concentrations of buffer and CDTA, were compared in order to determine the optimum conditions for the separation. The results are shown in Fig. 3. The graphs demonstrate that an increase in buffer, with constant CDTA, results in a decrease in the retention times of both species.

With buffer concentrations greater than 10.5 mmol/l, the vanadium(IV) elutes too close to the solvent front to be completely baseline resolved. On the other hand, a constant buffer with increasing CDTA also leads to a decrease in the vanadium(V) retention time, whereas the vanadium(IV) retention time stays constant. Both these influences were taken into account, and an eluant containing 20 mmol/l CDTA and 10.2 mmol/l buffer solution was chosen for all further investigations.

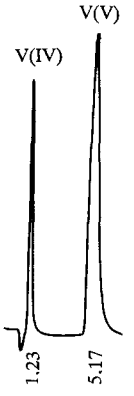

Fig. 2. Chromatogram of a sample containing 470 µg/ml V(IV) and 1000 µg/ml V(V). Conditions as in Table 1. Detection at 282 nm

3.3 Evaluation of the method

For the chosen optimum conditions, the analytical working range for vanadium(IV) and vanadium(V) was 0.5 to 20 µg/ml and 0.25 to 10 µg/ml, respectively. The detection limits, based on three times the standard deviation of the background, were calculated as 145 and 70 ng/ml, respectively.

In order to evaluate the feasibility of the method, the influence of 100 µg/ml of a variety of elements on the detection of 5 µg/ml of each of the two vanadium species were investigated. Synthetic samples containing the elements were prepared in a similar manner as the vanadium samples. Only a few metals interfere with the vanadium(IV) detection. The following elements were tested: (NaCl), F^-, NO_3^-, PO_4^{3-}, SO_4^{3-}, SCN^-, $S_2O_3^{2-}$, NH_4^+, Mn, Mg, Ni, Pb, Li, Hg, W(VI), Zn, Cu, Fe(III), Cr(III), Cr(VI), Ca, Bi, Ba, Be, Co and Cd. Interferences with V(IV) at 282 nm were caused by Hg, Cu, Fe(III), Cr(III), Cr(VI), Ca and Bi. In the case of V(V) only Cr(VI) interferes by forming a very broad peak, V(V) eluting on the Cr(VI) tail. V(V) can be detected in solutions containing up to ten-fold excess Cr(VI). Except for chromium(VI), all the interfering metals elute on the solvent front and therefore close to the vanadium(IV) peak. From the absorbance spectra in Fig. 1 it is apparent that vanadium(IV) absorbs slightly at 766 nm. Although the sensitivity of the vanadium(IV)-CDTA complex at this wavelength is much weaker, only a five-fold excess copper will interfere with the analysis. A wavelength of 766 nm should therefore be used for the detection of vanadium(IV) in solutions containing these interferences. The analytical working range for vanadium(IV) at this wavelength is 2 to 20 µg/ml, and the detection limit 500 ng/ml.

For samples containing these interfering metals, the following can be suggested:

a) Use a multi-channel detector, setting one channel at 282 nm and the other at 766 nm. Both vanadium species can then be detected with a single injection.
b) If only a single-channel detector is available, two injections will be necessary. As all the other conditions remain the same, it would be easy to switch between the wavelengths.

The method was applied to a number of synthetic samples (Table 2) and two industrial process samples

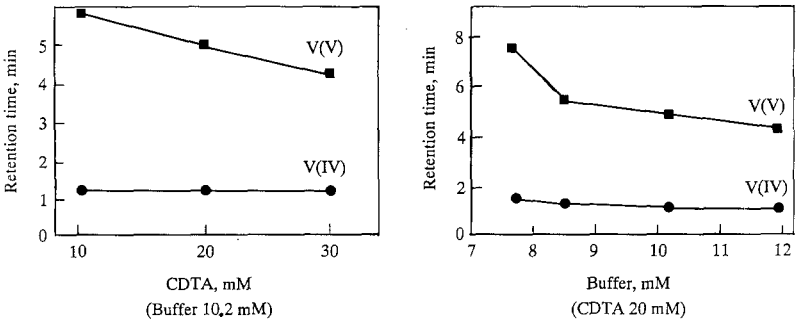

Fig. 3. Influence of eluant composition on retention times for vanadium(IV) and (V)

Table 2. Determination of vanadium species in synthetic and industrial process solutions. (Reproducibility was calculated from four to six replicate determinations.)

Sample no.	V(IV) (μg/ml)		V(V) (μg/ml)	
	added	found	added	found
1	182	180 ± 2,2	1600	1560 ± 10
2	100	105 ± 1,7	750	730 ± 6,4
3	370	360 ± 3,4	700	710 ± 4,2
4	633	630 ± 2,2	450	435 ± 3,1
5	575	560 ± 4,3	220	230 ± 1,9
6	333	325 ± 2,9	1000	960 ± 8,9
7	470	480 ± 3,6	340	355 ± 2,7
8	290	290 ± 1,7	460	485 ± 4,0
9	760	770 ± 4,8	160	155 ± 1,2
A	–	N.D.	–	1224 ± 9,0 1200(AAS)
A1	400	395 ± 2,8	–	1218 ± 8,9
B	–	N.D.	–	1192 ± 8,4 1180(AAS)
B1	400	398 ± 2,5	–	1170 ± 8,7

N.D. = Not detected
AAS = Atomic absorption spectroscopy

(A and B). Analysis of the latter samples showed that no vanadium(IV) was present. The total vanadium concentration in the two samples was verified by AAS. In order to test the effectiveness of the method for vanadium(IV) determination in more complex sample matrices and in the presence of the amount of vanadate shown, each sample was spiked with 400 μg/ml vanadium(IV) and re-analyzed (A1 and B1). From Table 2 it can be seen that there is a very good correlation between the real and experimental concentrations for both species.

Due to the simplicity of the overall chromatographic procedure (sample preparation, separation and detection), it would be easy to add an on-line concentration step to the system that would improve the detection limits by a factor of 2. This would make the technique applicable to trace analysis for environmental monitoring.

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