Vanadium speciation by chromatographic separation of V(IV) and V(V) in acidic solution followed by ICP-OES determination

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Abstract

A new method for vanadium speciation has been developed. The method is based on chromatographic separation of vanadium(IV) and vanadium(V) in acidic medium followed by the determination with ICP-OES. Vanadium species exist in acidic solution (pH < 3) as VO^{2+} for vanadium(IV) and VO_2^+ for vanadium(V). The two vanadium species were chromatographically separated using a cation exchange column, Dionex IonPack CG10, and eluant (120 mmol/ℓH_2SO_4) at a flow rate of 1.5 mℓ/min. The detection limits for vanadium(IV) and vanadium(V) are 40 µg/ℓand 30 µg/ℓ, respectively. Among common anions, only nitrite, NO_2^- which may act as oxidant for vanadium(IV) and reductant for vanadium(V) can cause interference. Interference from common cations has not been observed for concentration levels not exceeding 40 mg/ℓ. The developed method has been successfully applied to the determination of vanadium(IV) and vanadium(V) in synthetic and minerals processing samples.

Keywords: vanadium speciation, chromatography, ICP-OES, cation exchange

Introduction

Vanadium plays an important part in the analytical, biological, and environmental fields due to its dual character. Its toxicity is slightly less than that of lead, cadmium, and mercury at trace level concentrations (Wuilloud et al., 2000) but it also has beneficial biochemical functions, such as insulin-like and anti-carcinogenic characteristics (De Cremer et al., 2002). Therefore, the determination of vanadium in the samples from polluted areas and in nutrition studies has received much attention. Moreover, the toxicity of the two most stable vanadium oxidation states, i.e. vanadium(IV) and vanadium(V) is different, with the +5 oxidation state being more toxic. In biological systems, it has been proved that vanadium(V) is a strong inhibitor of the Na- and K-adenosinetriphosphatase (ATPase) enzyme while vanadium(IV) is weak (Minelli. et al., 2000). In the industrial field, one of the important roles of vanadium is its catalytic property in manufacturing processes, such as the contact process for the manufacture of sulphuric acid, in which V_2O_5 has a catalytic function and is reduced to vanadium(IV), which does not function as the catalyst. Therefore, the determination of both vanadium species rather than the total vanadium(V) is important when correct evaluation of its toxicity and the health risks to humans as well as its functions in biological or industrial systems are required.

Inductively coupled plasma mass spectrometry (ICP-MS) (Garcia-Sanchez et al., 2004), spectrophotometry (Amin, 2003), spectrofluorometry (Gao et al., 2002), inductively coupled plasma optical emission spectrometry (ICP-OES) (Wuilloud et al., 2000; Wuilloud et al., 2002), catalytic (Okamura et al., 2001; Shiobara et al., 1999) and electrochemical (Jen et al., 1997) methods have been successfully applied for the determination of vanadium in environmental, industrial, and biological samples. Most earlier methods were focused on determining one of the two vanadium species, i.e. the most stable vanadium(V). During the past decade, however, interest has shifted from the determination of total vanadium to the measurement of the two stable vanadium species. EDTA (ethylenediaminetetraacetic acid) has been widely used for vanadium speciation because it forms stable complexes with the two vanadium species allowing chromatographic separation. Reversed-phase liquid chromatography with a C8 column has been selected as the separation system for vanadium(IV) and vanadium(V) by using a tertiary eluant containing EDTA by several researchers (Colina et al., 2005; Wann and Jiang , 1997). EDTA was also used as a trapping agent for both vanadium(IV) and vanadium(V) by Minelli et al.(2000) for vanadium speciation in natural water. Ahmed and Banoo (Ahmed and Banoo, 1999) have developed a two-step method for vanadium speciation. A mixture of the two species was first masked by tartrate and then 1,5-diphenylcarbohydrazide (DPCH) was added to form a red-violet chelate of vanadium(V). The chelate was measured for the determination of vanadium(V) concentration. Vanadium(IV) concentration was obtained by the subtraction of the vanadium(V) concentration from the total vanadium concentration. Another similar two-step method has been proposed by Filik et al. (2004) by using CDTA (1,2-cyclohexylenedinitrilo)tetraacetic acid) as masking reagent for V(IV) instead of DPCH. Vanadium(V) was measured after the complexation with PAR (4-(2-pyridylazo)resorcinol), total vanadium concentration was obtained by the same method after the oxidation of vanadium(IV) to vanadium(V). The difference between the total vanadium concentration and the vanadium(V) concentration was the concentration of vanadium(IV). The two vanadium EDTA-complexes can be separated by a Dionex anion exchange column (Coetzee et al., 2002) or by a fused-silica capillary column modified with hexadecyltrimethylammonium bromide (Jen et al., 1997). A two-column separation of vanadium(IV) and vanadium(V) in acidic solution followed by catalytic detection (Okamura et al., 2001) has been developed. One column loaded with an acetylacetone-immobilised resin was used to collect vanadium(V) at pH 2.2-3.8 while

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another column loaded with an 8-quinolinole-immobilised resin was used to retain vanadium (IV). The retained two species can be successively eluted by diluted hydrochloric acid.

It was clear from the literature study that almost all developed methods for vanadium speciation are limited to separate the two vanadium species as their chelating complexes. No methods are reported where the two vanadium species are separated in the physico-chemical form in which they occur in the sample. Vanadium(V) is the most stable species but vanadium(IV) is easily oxidised to vanadium(V) in high pH value solutions. It can, however, be stable for months at low pH value. In the waste fluid from plants in which vanadium compounds have been used as catalysts the pH is often acidic. The two vanadium species may therefore co-exist in these fluids. In the analyses of vanadium in solid samples, acids are frequently used as the extractants, causing the extracts to support both vanadium(IV) and vanadium(V) in their physico-chemical forms. In view of these facts, it was considered necessary to develop a new method to directly separate and determine both vanadium species in the chemical forms in which they exist in acidic solutions. The purpose of this work was therefore to develop a fast and effective method based on cation exchange ion chromatography coupled with ICP-OES for the direct vanadium speciation analysis in the acidic media.

Experimental

Reagents and water

1 000 mg/ℓ vanadium(IV) and 1 000 mg/ℓ vanadium(V) stock solutions were prepared by dissolving a certain amount of $VOSO_4 \cdot 5H_2O$ (Merck, Germany) and NH_4VO_3 (Aldrich Chemical Company Inc., USA) in 20 mmol/ℓ H_2SO_4, respectively. 4 000 mmol/ℓ H_2SO_4 stock solution was prepared from 98% H_2SO_4 (Promark Chemicals, Batch No. BX090904, South Africa) in deionised water and then filtered through a 0.45 μm membrane filter. Filtered deionised water was obtained from a Milli-Q water purification system (Milllipore) with a resistivity of 18.2 MΩ.cm. All reagents were of analytical grade (AR). The samples or standards were prepared by properly diluting the stock solutions with deionised water.

The preparation of vanadium(V) stock solution was done by taking proper precautions. The vanadium(V) solution cannot be prepared by dissolving ammonium meta-vanadate in 20 mmol/ℓ sulphuric acid because at low pH (pH <2) and high concentrations, vanadate rapidly converts to vanadium pentoxide which has very low solubility in acidic solution and precipitates. Vanadium(V) stock solution was therefore prepared by dissolving ammonium meta-vanadate in hot water using sonication to increase the rate of dissolution. After complete dissolution of the compound, a measured amount of 4 000 mmol/ℓ sulphuric acid was added to the solution drop by drop to make the final solution contain 20 mmol/ℓ sulphuric acid.

Instrumentation

Separation was performed using a Dionex high-performance liquid chromatography (HPLC) system with a Dionex IonPack CG10 column at a flow rate of 1.5 mℓ/min and 120 mmol/ℓ H_2SO_4 as eluant. The sample size for a single injection was 50 μℓ. The determination was conducted on an ICP-OES (Varian Liberty 110, Australia) equipped with a V-groove nebuliser. The operating conditions for ICP-OES are shown in Table 1.

TABLE 1
The ICP-OES operating conditions

Determination wavelength	309.311nm
Viewing height	8 mm
Search window	0.040 nm
Filter	1
Order	1
PMT	650 V
Power	1.20 kW
Plasma gas flow rate	13.5 ℓ/min
Auxiliary gas flow rate	1.50 ℓ/min
Pump speed	30.0 r/min
Nebuliser pressure	150 kPa

Working principle

In acidic solution, vanadium(IV) exists as the cationic form, VO^{2+}. Although vanadium(V) exists as anionic vanadate or poly-vanadates at high pH value, it can be changed to the cationic dioxo-vanadium(V) ion (VO_2^+) at low pH conditions (pH~3 or lower) according to the following equilibrium:

$$[H_4V_{10}O_{28}]^{2-} \rightleftharpoons VO_2^+$$

If the pH value is controlled at lower than 3, the two vanadium species are cationic and can be separated by cation exchange columns. Vanadium(V) elutes first, followed by the vanadium(IV).

Results and discussion

The stability of vanadium(IV)

At low pH value (pH~3 or lower) and low concentration, vanadium(V) exists as the relatively stable dioxo-vanadium(V), VO_2^+. By contrast, vanadium(IV) is only stable at pH 2 or lower. It is gradually oxidised at pH 5~6 and rapidly oxidised to vanadium(V) by air at pH ≥ 9 (Bailar et al., 1973). In order to prevent the oxidation of vanadium(IV), vanadium(IV) solutions are prepared in 20 mmol/ℓ H_2SO_4 (pH<2). Experimental results show that, in 20 mmol/ℓH_2SO_4 solution, the oxidation of vanadium(IV) was not observed in three months. Therefore, all vanadium species, including vanadium(IV) and (V) are prepared in 20 mmol/ℓH_2SO_4 solution, in which they are all stable and cationic and ready for analysis.

Optimisation of LC conditions

The choice of eluant

To keep the stability of vanadium(IV), the eluant should be at low pH value (<2) and non-oxidative. In order to obtain such a low pH value, only strong mineral acids may be suitable for the purpose. Among the common mineral acids, nitric acid is oxidative and cannot be used as the eluant. Of the two strong mineral acids, sulphuric acid and hydrochloric acid, the latter has a lower elution ability than that of sulphuric acid when their concentrations are the same. Therefore, sulphuric acid was chosen as the eluant. Table 2 shows the change in the retention time and resolution with the change in sulphuric acid concentration.

Results show that the concentration of sulphuric acid

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TABLE 2
The change of retention time and resolution with the change of sulphuric acid concentration CG10 column. Flow rate: 1.5 mℓ/ℓ

Concentration (mmol/ℓ)	V(V) Retention time (min)	V(IV) Retention time (min)	Resolution
80	0.531	2.259	4.8
100	0.512	1.638	3.6
120	0.513	1.236	2.5
140	0.479	1.052	2.1
160	0.528	1.006	1.5

only slightly affected the elution of vanadium(V) but seriously affected the elution of vanadium(IV). Vanadium(IV) could not be eluted within 10 min when 20 mmol/ℓ sulphuric acid was used as the eluant for a CG10 column. The two peaks were overlapping when 250 mmol/ℓ sulphuric acid was used while the retention times for vanadium(V) only changed from 0.667 min to 0.508 min. Whether some multi-charged cations can affect the elution of the two species has been further examined experimentally. The common multi-charged cations, as well as a strong eluting ion, Mg^{2+} have been chosen for this experiment. Mg^{2+} added to a low concentration of sulphuric acid decreased the elution time for vanadium(IV) species, but caused high-emission backgrounds due to its emission line at 309.299 nm, close to the vanadium emission line of 309.311 nm. It also resulted in the broadening and overlapping of the peaks. Sulphuric acid without addition of Mg^{2+} was therefore chosen as eluant.

The choice of a suitable column for the separation

Two cation exchange columns were tested. The Dionex CG10 column produced a good separation for vanadium(IV) and vanadium(V) by using 120 mmol/ℓ H_2SO_4 or 160 mmol/ℓH_2SO_4 as eluant at a flow rate of 1.5 mℓ/min (the resolution for the separation was larger than 1.5). The Dionex CG12A column with 120 mmol/ℓ H_2SO_4 or 160 mmol/ℓH_2SO_4 as the eluant, however, caused partial overlapping of the peaks. Therefore, the CG10 column has been chosen for this study.

Optimisation of the eluant concentration and flow rate

As mentioned above, the concentration of sulphuric acid only slightly affected the elution of vanadium(V), which eluted first but seriously affected the elution of vanadium(IV). At the same flow rate, the higher the eluant concentration, the shorter the retention time for vanadium(IV) and the quicker the analysis. Experiment results given in Table 3 show that at the same concentration level, although high flow rate reduced both of the retention times for V(IV) and V(V), it also reduced the peak widths, making the resolution remain nearly unchanged. Peak areas were only slightly reduced with the increase in flow rate.

The results given in Table 3 show the expected decrease in retention time with increasing flow rate and the reduction in peak area. The overlapping of peaks at high flow rate has also been observed experimentally, especially for the measurement of the two species with high concentration. A medium flow rate of 1.5 mℓ/ℓ was therefore chosen for analyses. The optimised IC conditions are summarised in Table 4.

TABLE 3
The variation of peak parameters with the flow rate CG 10 column: Eluant: 120 mmol/ℓ H_2SO_4; injection size: 50 µℓ;sample: the mixture of 10 mg/ℓ V(IV) and 10 mg/ℓ V(V)

Flow rate (mℓ/min)	Vanadium(V)			Vanadium(IV)			Resolution
	RT (min)	PW (s)	PA	RT (min)	PW (s)	PA	
1.1	0.649	13.3	14 306	1.608	14.6	13 907	2.4
1.3	0.576	10.3	14 226	1.411	12.3	12 590	2.6
1.5	0.513	9.1	13 016	1.236	11.2	11 615	2.5
1.7	0.467	7.7	12 827	1.113	8.9	11 393	2.7

RT: retention time. PW: peak width. PA: peak area.

TABLE 4
The optimised IC operation conditions

Separation column	CG10
Eluant	120 mmol/ℓ H_2SO_4
Flow rate	1.5 mℓ/ℓ
Injection size	50 µℓ

Detection limits

The detection limits for vanadium(IV) and vanadium(V) were 40 µg/ℓ and 30 µg/ℓ, respectively. The quantitative detection limits, at which the two species can quantitatively be integrated by the software used, were 0.2 mg/ℓ and 0.1 mg/ℓ; for vanadium(IV) and V(V), respectively. The detection limit of vanadium(V) is lower than that of vanadium(IV) because vanadium(V) elutes first and the consequently narrower peak makes the integration easier and more accurate.

Interference study

Anion interference

The emission lines for non-metals are far away from the chosen emission line of vanadium, and spectral interferences from common anions can therefore be neglected. Anions may, however, cause chemical interference through chemical reactions, such as precipitation, redox reactions, and complexation. Precipitation could result not only in the loss of vanadium but also causes the blockage of the column. Redox reactions will change one vanadium species to another, reducing the reliability of the determination, while complexation of vanadium species causes changes in retention times because the charge and structure change.

The common anions, F^-, Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, Ac^-, $C_2O_4^{2-}$ have been studied. Neither precipitation nor complexation has been observed during the study at concentrations as high as 200 mg/ℓ for each anion, probably due to the low pH of the sample, at which the complexes and precipitates are not likely to form.

Cation interferences

Among cations, only magnesium at the emission line of 309.299 nm and chromium at the emission line of 309.349 nm may cause potential spectral interferences at the vanadium emission line of 309.311 nm. The potential interference from chromium can be avoided by an appropriate narrowing of the search window. Interference from magnesium on vanadium(IV) may be serious when its concentration is high because of the proximity of its emission line and the retention

of Mg^{2+} (1.559 min) which is close to that of VO^{2+} under the selected IC conditions. Table 5 lists the experimental results for the interference from magnesium.

TABLE 5
Interference from magnesium

	V(IV) Peak area
4 mg/ℓV(IV) only	8 157 ± 328 (max: 8485)
4 mg/ℓV(IV) with 10 mg/ℓ Mg	8 750 ± 328 (min: 8422)
4 mg/ℓ V(IV) with 40 mg/ℓ Mg	8 894 ± 254 (min: 8640)

The results show that magnesium does cause some interference in the determination of vanadium(IV) when its concentration is as high as 40 mg/ℓ. If the magnesium concentration in samples is higher than 40 mg/ℓ, the interference from magnesium can be easily eliminated by changing the analytical line of vanadium from 309.311 nm to 310.230 nm, at which magnesium can not give any interference to the determination of vanadium.

Ratio interference

The maximum concentration ratios of the vanadium species for quantitative determination are summarised in Table 6. The V(V)/V(IV) ratio was obtained by fixing the V(IV) concentration at 1 mg/L but changing the concentration of V(V). The V(IV)/V(V) ratio was obtained by fixing the V(V) concentration at 1 mg/ℓ but changing the concentration of V(IV).

TABLE 6
The ratio of interference from the concentration ratio of V(IV) and V(V)

Ratio	Conclusion
V(V)/V(IV) ≤12	Quantitative results for both species
25>V(V)/V(IV) >12	Quantitative results for V(V) but qualitative results for V(IV)
V(IV)/V(V) ≤ 8	Quantitative results for both species
20>V(IV)/V(V)>8	Quantitative results for V(V) but qualitative results for V(IV)

Applications of the developed method

The determination of vanadium in synthetic samples

The results of the determination of synthetic samples are shown in Table 7.

TABLE 7
The determination of vanadium in synthetic samples

Sample No	V(V)			V(IV)		
	Known (mg/ℓ)	Measured (mg/ℓ)	Recovery (%)	Known (mg/ℓ)	Measured (mg/ℓ)	Recovery (%)
1	0.1	0.13 ±0.02	130	0.2	0.21±0.02	105
2	0.2	0.21±0.03	105	0.4	0.44±0.03	110
3	0.4	0.37±0.10	93	0.8	0.82±0.03	102
4	0.8	0.77±0.04	96	2.0	2.01±0.01	100
5	2.0	2.01±0.04	100	4.0	3.99±0.08	99.8
6	5.0	5.41±0.27	108	8.0	7.90±0.42	98.8
7	10.0	10.40±0.16	104	20.0	20.04±0.28	100

For the synthetic samples, the measured results show excellent consistency with the known concentration. The recovery for the synthetic samples ranges from 93% to 110% except for 0.1 mg/ℓ vanadium(V) where the recovery was 130%. This is caused by the low concentration of vanadium(V) which is close to the quantitative detection limit of vanadium (V) by this method.

The determination of vanadium species in a minerals processing matrix

A minerals processing sample, with unknown vanadium speciation, was obtained from GRD Minproc. The composition of the sample was as follows: U_3O_8, 841 mg/ℓ (equivalent to about 713 mg/ℓ uranium); V_2O_5, 234 mg/ℓ (equivalent to about 131 mg/ℓ); CO_3^{2-}, 20g/ℓ(~333 mmol/ℓ); Cl^-, 0.55 g/ℓ (~15 mmol/ℓ); SO_4^{2-}, 1.2 g/ℓ (~12.5 mmol/ℓ); and pH, ~10. Pre-analyses of the sample were performed by ICP-OES before the speciation determination to check for any major element that could cause interference. More than 20 elements were measured. It was found that in addition to uranium, only sodium was present in the sample at high concentration levels of about 17 mg/ℓ. The other elements, including the possible interfering element of magnesium, were present at trace level. The pH of the sample was 10.7. The total concentration of vanadium was determined by ICP-OES using the dilution (10x- 100x- and 1 000x dilution) and standard addition methods. The results are shown in Table 8.

TABLE 8
The measurement of total vanadium concentration in the real sample

Methods used for the determination	Total vanadium concentration (mg/ℓ)
10-time dilution of the sample	19.43
100-time dilution of the sample	1.98
1000-time dilution of the sample	0.21
standard addition (100-time dilution)	1.96

The dilution method and the standard addition method both gave consistent results for the total vanadium concentration confirming absence of matrix effects during the determination.

According to the measured pH value, the sample is in a matrix of strong alkalinity. Vanadium(IV) species in the strong alkaline solution would therefore be oxidised rapidly and the sample was not expected to contain measurable quantities of vanadium(IV).

For column separation the sample needed prior filtration to prevent column blockage. To check whether filtration could affect the vanadium concentration, an unfiltered 10x diluted sample and filtered 10x diluted sample were analysed by ICP-OES. The determined results are listed in Table 9.

TABLE 9
The determination of total V in the sample before and after filtration

Sample	Total vanadium concentration (mg/ℓ)
Unfiltered 10-time dilution sample	19.43 ± 1.02
Filtered 10-time dilution sample	19.14 ± 0.97

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Because acidic samples (pH < 3) are required for separation of the V species, the sample was acidified before analysis. To reduce matrix effects and to obtain the optimum separation of the two species, the sample was diluted 10x to give a final concentration of around 20 mg/ℓ. Too high concentrations may cause peak overlap. The sample preparation procedure was: 5 mℓ filtered original sample was transferred to a 50 mℓ volumetric flask, and then acidified and diluted with 0.5 mol/ℓ sulphuric acid to the mark. The prepared sample had a pH range of between 1 and 2, where vanadium(IV) and vanadium(V) exist as VO^{2+} and VO_2^+, respectively. 50 µℓ sample was injected into the CG10 column and the eluted vanadium species determined by ICP-OES. Vanadium(V) was measured at the concentration of 21.52 ± 1.03 mg/ℓ, but vanadium(IV) was not detectable. Vanadium(V) therefore accounts for the total vanadium concentration of 215.2 ± 10.3, which is consistent with the total vanadium concentration, as shown in Table 8.

To verify the measured result for the sample, the standard addition method was applied. The sample was diluted 100 times and spiked with different concentrations of vanadium species. The concentration of vanadium(V) was calculated as 2.26 mg/ℓ and the concentration of vanadium(IV) as 0.018 mg/ℓ, which is below the detection limit. The measured results for vanadium(IV) and vanadium(V) were therefore consistent with the previous determination.

To demonstrate the effectiveness of the proposed IC-ICP-OES method to determine V species in mineral-processing samples, samples spiked with different concentration ratios of V(IV) and V(V) after 100x dilution, were analysed. The results are given in Table 10.

Excellent consistency between the spiked concentrations and measured results has been obtained by the method.

Conclusion

A new IC-ICP-OES method has been developed to separate and determine vanadium (IV) and vanadium(V) in the acidic medium. The method not only determines vanadium(IV) and vanadium(V) in acidic solution, but can also be used to separate vanadium species in alkaline solution after acidification of the sample. The method is fast and effective and almost interference-free. Only magnesium could interfere with the determination of vanadium(IV) when its concentration is higher than 40 mg/ℓ. The successful determination of vanadium(IV) and vanadium(V) in synthetic samples and a minerals processing sample with a relatively complex matrix indicates the usefulness of this method.

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TABLE 10
Recoveries for 100x diluted sample spiked with different concentration ratios of V(IV) and V(V)

Sample No	V(IV)			V(V)			
	Spiked (mg/ℓ)	Measured (mg/ℓ)	Recovery (%)	Spiked (mg/ℓ)	Total* (mg/ℓ)	Measured (mg/ℓ)	Recovery (%)
1	20	20.03±0.12	100	0	2.15	2.03±0.07	94
2	3	2.76±0.32	92	20	22.15	21.94±0.17	99
3	10	10.10±0.07	101	10	12.15	12.20±0.10	100
4	5	5.25±0.37	105	15	17.15	17.14±0.47	100
5	15	14.86±0.02	99	5	7.15	7.13±0.20	100
6	0	Undetectable		2	4.15	3.97±0.01	96

** Total concentration of V(V) after spiking*

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