# Method for Vanadium Speciation in Aqueous Samples by HPLC-ICP-OES

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ABSTRACT

**A method for vanadium speciation is proposed. The method uses a low concentration eluent, 10 mmol $L^{-1}$ EDTA and 14 mmol $L^{-1}$ sodium carbonate, for the ion chromatographic separation of vanadium species at a flow rate of 1.2 mL $min^{-1}$. The quantitative detection limits were 0.14 mg $L^{-1}$ for V(IV) and 0.20 mg $L^{-1}$ for V(V) using ICP-OES detection. The method was successfully applied to the analysis of synthetic samples and mineral processing samples.**

KEYWORDS

**Anion exchange, vanadium speciation, EDTA, HPLC, ICP-OES.**

## 1. Introduction

Speciation of vanadium is of great importance because vanadium species are both essential and toxic to humans[1] and occur in many industrial and mineral processes where accurate data regarding species concentrations are required. Low concentrations of vanadium ($\mu$g $L^{-1}$ level) are regarded as essential for cell growth while at higher concentrations (mg $L^{-1}$) it becomes toxic.[2] The environmental pollution by vanadium is caused by many industrial processes, such as occur in the steel industry, chemical industry, petrochemical industry, and especially the phosphate industry.[3] In addition, the combustion of fossil fuels, such as crude petroleum, oils, and certain coals and lignite are other sources of vanadium release into the environment. Vanadium can occur in the +4 or +5 oxidation states in the environment although vanadium has other oxidation states. Vanadium(V) species are the most toxic. Redox reactions between the two vanadium species may occur under proper environmental conditions. Therefore, the total concentration of vanadium or the concentration of only one vanadium species cannot fully reflect the potential hazards of vanadium and could lead to an incorrect assessment of vanadium pollution.

Many methods have been developed for the determination of vanadium in a variety of sample matrix types, but most of these methods can only measure the total concentration of vanadium, or one of the two vanadium species, particularly V(V).[4–6] Some two-step methods for the determination of the two vanadium species[7–10] have been proposed by several groups. These methods normally measure one of the two species in one step, and in the other step, the total concentration. The concentration of the other species can be obtained by subtracting that of the first species from the total. Although these methods can obtain low detection limits and good analytical results, they are laborious and time-consuming. In another method, Bosque-Sendra *et al.*[11] detected V(IV) as V(IV)-ECR (eriochrome cyanine R) complex, while the V(V) determination was performed by its ascorbic acid reduction to V(IV) and then complexation with ECR after the V(IV)-ECR had been separated. Several methods have been developed to determine both V(IV) and V(V). In these methods, EDTA was widely used as a complexing agent to form complexes with V(IV) and V(V), which can be separated by a normal anion exchange column,[12] or by a modified fused-silica capillary column,[13] or by C8 reversed phase column,[14,15] followed by different detection systems. Separation of V(IV) and V(V) without any complexation prior to separation has been proposed.[3] In this method, the two species can be separated at pH 3.2 on an anionic exchanger containing AMTS (3-aminopropyltrimethoxysilane). Under these circumstances, V(IV), existing as $VO^{2+}$, was not retained, while V(V), existing as $H_2VO_4^-$ was partly retained; the separation was produced by the difference in the retention on the exchanger. The separation of V(IV) and V(V) by C8 reversed phase column[14,15] was susceptible to many factors, such as pH, the concentrations of the ion-pair agents, flow rate, temperature, etc., so that the operating conditions are required to be carefully optimized. Column equilibration requires a long time. The capillary zone electrophoresis separation[13] is definitely time-consuming and not suitable for the determination of low concentration samples due to its high detection limits.

In our previous work an interference-free method[12] based on anion exchange separation of V(IV)- and V(V)-EDTA complexes and determination by ICP-OES was developed. This method, however, had relatively poor limits of quantitative determination, making it unsuitable for analysing environmental samples. Other disadvantages were the high elution flow rates, high eluent strength and high salinity of the eluent. These conditions are not ideal for prolonged nebulization and plasma atomization. The purpose of this work was therefore to modify the method for vanadium speciation so as to reduce the eluent salinity and eluent strength, and to improve the limits of quantitative determination, using IC-ICP-OES.

## 2. Experimental

The separation of vanadium species was done with a Dionex AG5 anion exchange guard column in conjunction with a Dionex gradient pump. An inductively coupled plasma optical emission spectrometer (Varian Liberty 110) was used as detector. The ICP-OES conditions are shown in Table 1.

The stock solutions of 200 mmol $L^{-1}$ EDTA and 500 mmol $L^{-1}$ sodium carbonate were made up by dissolving 18.612 g of EDTA (disodium ethylenediaminetetraacetate, SMM Chemicals (Pty) Limited, Johannesburg, South Africa), and 26.4975 g of sodium

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**Table 1** The main ICP-OES conditions for the determination of vanadium.

| | |
|---|---|
| Wavelength | 309.311 nm |
| Search window | 0.040 nm |
| Grating order | 1 |
| PMT voltage | 650 V |
| Power | 1.20 kW |
| Main gas flow | 15.0 L $min^{-1}$ |
| Auxiliary gas flow | 1.50 L $min^{-1}$ |

carbonate (anhydrous, BDH Chemicals Ltd., Poole, England) with deionized water in 250 mL and 500 mL volumetric flasks, respectively. 1000 mg $L^{-1}$ V(IV) and 1000 mg $L^{-1}$ V(V) stock solutions in 20 mmol $L^{-1}$ EDTA were prepared by dissolving 0.2484 g of hydrated vanadium(IV) oxide sulphate ($VOSO_4 \cdot 5H_2O$, Merck, Darmstadt, Germany), and 0.1148 g of ammonium metavanadate ($NH_4VO_3$, Aldrich Chemical Company, Inc., Milwaukee, USA) with deionized water and 5 mL of 200 mmol $L^{-1}$ EDTA in two 50 mL flasks, respectively. The function of EDTA in the stock solutions was to form anionic complexes with V(IV) and V(V) and to stabilize V(IV). The standards or the samples with known concentrations were obtained by dilution of the stock solutions with 5 mmol $L^{-1}$ EDTA solution. The two anionic vanadium-EDTA complexes, existing as $[VO(EDTA)]^{2-}$ for V(IV) and $[VO_2(EDTA)]^{3-}$ for V(V), can be separated by an anion exchange column. V(IV)-EDTA complex elutes first, followed by the V(V)-EDTA complex. All reagents used in this experiment were of analytical reagent grade. All solutions were filtered with 0.45 $\mu$m membrane to protect columns from particulate blockages.

## 3. Results and Discussion

### 3.1. Liquid Chromatography Operating Conditions

3.1.1. *Eluent Composition*

The recommended eluent for the AG5 column is a mixture of carbonate and bicarbonate. However, without the addition of EDTA to the eluent, it is very difficult to elute V(V)-EDTA complex from the column, while the retention time for V(IV)-EDTA complex is longer than one minute. This means that EDTA in the eluent plays a vital role for the elution of V(IV) as well as for V(V). The high elution capability of EDTA for V(V) is due to its ionization in basic solution to form strong eluting ions, such as $EDTA^{3-}$ or even $EDTA^{4-}$, to replace the $[VO_2(EDTA)]^{3-}$ on the exchange sites in the column. The carbonate and bicarbonate in the eluent only supply a basic environment in which EDTA can be ionized to more negative ions. This hypothesis is confirmed by using sodium hydroxide instead of the mixture of carbonate and bicarbonate. Similar elution for V(IV) and V(V) was obtained although hydroxide is a weaker eluting ion than carbonate. The higher the alkalinity of the eluent, the shorter the retention time for vanadium species. Bicarbonate was therefore excluded from the eluent. The modified eluent for the separation of V(IV) and V(V) was therefore a mixture of carbonate and EDTA.

3.1.2. *Eluent Flow Rate*

The effect of eluent flow rate on peak parameters was studied. The results are given in Table 2. The results in Table 2 show that the peak area (PA) and retention time (RT), especially V(V) retention time, increase with decrease in flow rate. The half peak width (HPW), which is almost proportional to the difference between the retention times of the two species, increases with decrease in flow rate as well. Therefore the resolution does not change significantly with the flow rate. Although high flow rates give shorter retention times, they always result in low peak areas. As the flow rate is decreased from 1.8 mL $min^{-1}$ to 1.5 mL $min^{-1}$, the retention time for V(V), which controls the analysis time, is increased by 16% and the peak areas for V(IV) and V(V) are increased by 12% for both species. As the flow rate is decreased from 1.5 mL $min^{-1}$ to 1.2 mL $min^{-1}$, the retention time for V(V) is increased by 19% and the peak areas for V(IV) and V(V) are increased by 21% for V(IV) and 26% for V(V). As the flow rate decreases from 1.2 mL $min^{-1}$ to 0.9 mL $min^{-1}$, the retention time for V(V) is increased by 39%, but the peak areas for V(IV) and V(V) are increased by only 16% for V(IV) and 17% for V(V). Therefore, to find a suitable compromise between short retention time and large peak area, a flow rate of 1.2 mL $min^{-1}$ was chosen for further study.

3.1.3. *Eluent Strength*

When the eluent strength is too low, the peak area for V(V) is reduced dramatically while the analysis time is very long. Too high eluent strength also reduces the peak areas. The results can be viewed in Table 3. These results are explained by the very broad peak of V(V) at low eluent strength and by peak overlapping at high eluent strength. It can be estimated that if the alkalinity of the eluent is high, i.e. the carbonate concentration is high enough, even the eluent containing low concentration of EDTA can still give a good separation of the two species. The experimental results show that if the EDTA concentration is lower than 10 mmol $L^{-1}$, the sensitivity of V(V) is reduced considerably, while if the concentration of EDTA is higher than 10 mmol $L^{-1}$, the peak areas for both species remain almost constant. Therefore, 10 mmol $L^{-1}$ EDTA was fixed in the eluent. If the concentration of $Na_2CO_3$ in the eluent is too high it leads to poor separation, while too low a concentration results in long analysis times. The optimized eluent conditions were therefore taken as 14 mmol $L^{-1}$ carbonate plus 10 mmol $L^{-1}$ EDTA. The optimum IC conditions are given in Table 4.

### 3.2. Quantitative Detection Limits

The quantitative detection limits were obtained by successively reducing the concentrations of the two vanadium species to values at which the quantitative results can be obtained. Accord-

**Table 2** The effect of flow rate on peak parameters. Eluent: a mixture of 20 mmol $L^{-1}$ EDTA and 16 mmol $L^{-1}$ $Na_2CO_3$.

| Flow rate/mL $min^{-1}$ | Resolution | V(IV) | | | V(V) | | |
|---|---|---|---|---|---|---|---|
| | | RT/min | PA | HPW/s | RT/min | PA | HPW/s |
| 1.8 | 2.1 | 0.472 | 5107 | 6.6 | 1.068 | 4411 | 13.1 |
| 1.5 | 2.3 | 0.540 | 5728 | 6.8 | 1.243 | 4955 | 14.9 |
| 1.2 | 2.5 | 0.634 | 6932 | 7.3 | 1.482 | 6241 | 17.0 |
| 0.9 | 2.6 | 0.869 | 8077 | 9.8 | 2.065 | 7338 | 22.9 |
| 0.6 | 2.4 | 1.253 | 8427 | 17.8 | 3.031 | 7451 | 35.4 |

**Table 3** The effect of eluent strength on the sensitivity of vanadium measurement. Sample: 10 mg $L^{-1}$ V(IV) and 10 mg $L^{-1}$ V(V) in 5 mmol $L^{-1}$ EDTA; AG5 column; 1.2 mL $min^{-1}$.

| Eluent | V(IV) | | V(V) | |
|---|---|---|---|---|
| | Peak area | Retention time/min | Peak area | Retention time/min |
| 4 mM $Na_2CO_3$, 5 mM EDTA | 7358 | 0.879 | 6160 | 4.570 |
| 8 mM $Na_2CO_3$, 10 mM EDTA | 7547 | 0.731 | 6835 | 2.600 |
| 12 mM $Na_2CO_3$, 15 mM EDTA | 7562 | 0.744 | 7081 | 2.067 |
| 16 mM $Na_2CO_3$, 20 mM EDTA | 7532 | 0.697 | 6909 | 1.700 |
| 20 mM $Na_2CO_3$, 25 mM EDTA | 7347 | 0.669 | 6659 | 1.453 |

**Table 4** The optimum IC operating conditions.

| | |
|---|---|
| Column | AG5 |
| Eluent | 10 mmol $L^{-1}$ EDTA and 14 mmol $L^{-1}$ $Na_2CO_3$ |
| Flow rate | 1.2 mL $min^{-1}$ |
| Injection size | 50 $\mu$L (mg $L^{-1}$ level) |

ing to the above procedure, the quantitative detection limit for V(IV) is 0.14 mg $L^{-1}$, while the detection limit for V(V) is 0.20 mg $L^{-1}$. When the concentrations are lower than the above values, the peak areas for the two species are difficult to integrate.

### 3.3. Interference Study

According to our previous study,[12] only the nearby Nb line at 309.418 nm can interfere with the determination of vanadium at the wavelength of 309.311 nm. But a high concentration of Nb is not expected in the samples due to its very low content on the Earth. Al can only give interference, especially for V(V), when its concentration is higher than 100 mg $L^{-1}$, but such a high concentration of Al in the environmental samples is not expected. Interferences from common anions, such as $F^-$, $Cl^-$, $Br^-$, $Ac^-$, $NO_2^-$, $NO_3^-$, $SO_4^{2-}$, and $HPO_4^{2-}$ were not observed when their concentrations were as high as 200 mg $L^{-1}$. For environmental samples, this method is interference-free due to low element and ion concentrations. The two species of vanadium can interfere with each other when the ratio of the two species is too large. A complete study of the ratio interference has been accomplished and the results are shown in Table 5.

## 4. Application of the Method

### 4.1. Working Range

The working range is defined arbitrarily by the authors as the determination concentration range, which ranges from the detection limit to 50 mg $L^{-1}$ for V(IV) or from the detection limit to 60 mg $L^{-1}$ for V(V) when the concentration ratio does not cause interference to the determination of both species; or as the determination concentration range, within which the maximum concentration ratios of the two species do not exceed the values shown in Table 5, and the maximum concentrations do not exceed 50 mg $L^{-1}$ for V(IV) and 60 mg $L^{-1}$ for V(V).

**Table 5** The ratio interference of V(IV) and V(V).

| Ratio | | Description |
|---|---|---|
| V(V)/V(IV) | ≤20 | Quantitative results for both species; recovery of V(IV) no less than 90% |
| | >20 | The recovery of V(IV) is less than 90% |
| V(IV)/V(V) | ≤16 | Quantitative results for both species |
| | >16 | The measurement of V(V) was seriously affected. |

### 4.2. Determination of Synthetic Samples

This method has been applied to the determination of vanadium species in synthetic samples with increasing concentrations of each vanadium species and with varying concentration ratios. The experimental results are given in Tables 6, 7 and 8. The experimental results show that as long as the concentrations of the samples and the concentration ratios are within the working range, the measured results give excellent agreement with the known concentrations. Even at the sub-mg $L^{-1}$ level, reliable results were still obtained. These experimental results prove that this new method is suitable for the analysis of synthetic aqueous samples.

### 4.3. Determination of a Real Sample

A mineral processing sample from GRD Minproc has been analysed. The sample contained 713 mg $L^{-1}$ uranium, 333 mmol $L^{-1}$ $CO_3^{2-}$, and less than 15 mmol $L^{-1}$ $Cl^-$ and $SO_4^{2-}$, with a pH value of 10.7. Pre-analyses of the sample by successive dilution and the standard addition method were performed by ICP-OES. The concentration of total vanadium in the sample was determined as 196 mg $L^{-1}$. Matrix effects have been examined by comparison

**Table 6** Measurement of the samples with low concentrations.

| Sample no. | V(IV) | | | V(V) | | |
|---|---|---|---|---|---|---|
| | Known/ mg $L^{-1}$ | Measured/ mg $L^{-1}$ | Recovery/ % | Known/ mg $L^{-1}$ | Measured/ mg $L^{-1}$ | Recovery/ % |
| 1 | 0.20 | 0.25 ± 0.01 | 125 | 0.20 | 0.28 ± 0.04 | 140 |
| 2 | 0.50 | 0.49 ± 0.06 | 98 | 0.50 | 0.49 ± 0.09 | 98 |
| 3 | 0.80 | 0.80 ± 0.03 | 100 | 0.80 | 0.79 ± 0.03 | 99 |
| 4 | 1.00 | 0.99 ± 0.04 | 99 | 1.00 | 0.99 ± 0.05 | 99 |
| 5 | 2.00 | 1.99 ± 0.06 | 99.5 | 2.00 | 1.93 ± 0.17 | 97 |
| 6 | 5.00 | 4.95 ± 0.05 | 99 | 5.00 | 5.00 ± 0.07 | 100 |
| 7 | 10.00 | 10.03 ± 0.15 | 100 | 10.00 | 10.01 ± 0.03 | 100 |

**Table 7** Measurement of the samples with large dynamic concentration ranges.

| Sample no. | V(IV) | | | V(V) | | |
|---|---|---|---|---|---|---|
| | Known/ mg $L^{-1}$ | Measured/ mg $L^{-1}$ | Recovery/ % | Known/ mg $L^{-1}$ | Measured/ mg $L^{-1}$ | Recovery/ % |
| 1 | 0.30 | 0.33 ± 0.02 | 110 | 0.50 | 0.62 ± 0.04 | 124 |
| 2 | 3.00 | 3.00 ± 0.11 | 100 | 5.00 | 4.97 ± 0.44 | 99 |
| 3 | 20.00 | 20.07 ± 0.69 | 100 | 30.00 | 29.28 ± 0.80 | 98 |
| 4 | 30.00 | 29.75 ± 0.90 | 99 | 40.00 | 39.54 ± 1.27 | 99 |
| 5 | 40.00 | 40.15 ± 1.71 | 100 | 50.00 | 50.80 ± 1.94 | 102 |
| 6 | 50.00 | 51.18 ± 0.61 | 102 | 60.00 | 61.51 ± 0.17 | 102 |

**Table 8** Measurement of samples with varying concentration ratios.

| Sample no. | V(IV) | | | V(V) | | |
|---|---|---|---|---|---|---|
| | Known/ mg $L^{-1}$ | Measured/ mg $L^{-1}$ | Recovery/ % | Known/ mg $L^{-1}$ | Measured/ mg $L^{-1}$ | Recovery/ % |
| 1 | 0.50 | 0.52 ± 0.02 | 104 | 4.00 | 3.97 ± 0.14 | 99 |
| 2 | 32.00 | 31.47 ± 0.94 | 98 | 2.00 | 2.02 ± 0.09 | 101 |
| 3 | 4.00 | 4.50 ± 0.08 | 112 | 64.00 | 64.52 ± 0.98 | 101 |
| 4 | 60.00 | 60.08 ± 1.16 | 100 | 3.00 | 2.85 ± 0.14 | 95 |
| 5 | 50.00 | 50.29 ± 1.40 | 101 | 25.00 | 24.07 ± 0.50 | 96 |
| 6 | 20.00 | 21.24 ± 1.14 | 106 | 40.00 | 39.87 ± 0.47 | 100 |

**Table 9** Determination of the real sample spiked with different concentrations of V(IV) and V(V) after 50-times dilution.

| Sample | V(IV) | | | V(V) | | |
|---|---|---|---|---|---|---|
| | Spiked/ mg $L^{-1}$ | Measured/* mg $L^{-1}$ | Recovery/ % | Spiked/ mg $L^{-1}$ | Measured/* mg $L^{-1}$ | Recovery/ % |
| 1 | 2 | 2.09 ± 0.15 | 104 | 2 | 2.31 ± 0.25 | 116 |
| 2 | 5 | 4.71 ± 0.12 | 94 | 5 | 4.59 ± 0.50 | 92 |
| 3 | 10 | 10.32 ± 0.17 | 103 | 10 | 10.37 ± 0.64 | 104 |
| 4 | 15 | 14.91 ± 0.45 | 99 | 15 | 14.80 ± 0.82 | 99 |
| 5 | 20 | 19.97 ± 1.64 | 100 | 20 | 20.40 ± 1.32 | 102 |

* The measured concentration is the difference between the total concentration after spiking and the original sample concentration, i.e. the measured spiked concentration.

of the diluted sample (10-, 100- and 1000-times dilution) with the standard addition method. No matrix effects could be demonstrated. Experimental results show that the filtration does not affect the total concentration of vanadium.

At the pH of the sample (pH 10.7), V(V) is expected to be the main species of vanadium while V(IV) may not exist or exist in very low or undetectable concentrations because of the instability of V(IV) species in strong alkaline solution without any protection. The sample was filtered and then diluted 50 times with 20 mmol $L^{-1}$ EDTA. 50 $\mu$L of the diluted sample was injected to the AG5 column for the separation. The eluted vanadium complexes were determined by ICP-OES. Two peaks were observed. The first peak could only be recognized but not quantitatively integrated due to the low concentration of V(IV) and high ratio of V(V) to V(IV). Concentrations of V(IV) and V(V) were found to be 0.09 mg $L^{-1}$ and 4.15 mg $L^{-1}$ respectively, when applying the method of standard additions. The ratio of V(V) to V(IV) was 46, therefore much higher than the maximum ratio of 20 for accurate determinations, shown in Table 5. The concentration of the sample without dilution was 207.5 mg $L^{-1}$, consistent with the concentration of 196 mg $L^{-1}$ determined by ICP-OES.

The sample was spiked with different concentrations of V(IV) and V(V) after 50-times dilution. The determination results are given in Table 9. The experimental results shown in Table 9 indicate that the measured concentrations show good consistency with the spiked concentrations.

## 5. Conclusion

This study shows the applicability of the modified method to the simultaneous separation and determination of V(IV) and V(V) as EDTA complexes in aqueous samples by using a low concentration eluent and a low flow rate. By reducing the EDTA concentration to 10 mmol $L^{-1}$ instead of 20 mmol $L^{-1}$ and excluding $NaHCO_3$ in the eluent as in the previous method,[12] an improvement in the limits of quantitative determination of 14 and 20 times was obtained for V(IV) and V(V) respectively. The method is fast, cost-effective and interference-free and was shown to give excellent speciation results in difficult mineral processing matrices. The low salinity of the eluent would allow quadrupole-based ICP-MS to be used as the detection system after separation of the species as an alternative to ICP-OES, should lower detection limits be required.

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