The separation and simultaneous determination of V(IV) and V(V) species complexed with EDTA by IC-ICP-OES

PP Coetzee*, JL Fischer and Mingsong Hu
Department of Chemistry and Biochemistry, Rand Afrikaans University, PO Box 524, Auckland Park 2006, South Africa

Abstract

A method for the separation of V(IV) and V(V) in the form of the EDTA complexes using anion chromatography with a Dionex AG5 anion exchange guard column, and the simultaneous determination of V(IV) and V(V) by inductively coupled plasma optical emission spectrometery is described. The interference from other elements is negligible. The detection limits of V(IV) and V(V) were 0.02 mg/ℓ and 0.05 mg/ℓ, respectively, using a glass nebuliser and 2 µg/ℓ for both species by using an ultrasonic nebuliser. The linear range was two orders of magnitude. The method was applied to the analysis of spiked water and industrial samples containing V in different oxidation states.

Introduction

V(IV) and V(V) species play an important role in many industrial and environmental processes. V and its compounds are used extensively in the steel and petrochemical industries. The South African petrochemical industry, for example, uses the Sulfolin and Benfield processes, based on the V(IV)/V(V) redox couple to remove sulphur and CO_2, respectively, from process streams in the production of petrol and diesel from coal. Both species can exist in the environment but V(V) species are the most stable and also the most toxic (Browning, 1961; Cotton and Wilkinson, 1988). Other oxidation states such as V(II) and V(III) are not stable and will be oxidised to V(IV) and V(V) by atmospheric oxygen. Both V(IV) and V(V) species may find their way into the natural environment, in particular surface waters as toxic pollutants. V(IV) can be stabilised in natural waters by complexation with a variety of ligands, such as carboxylic acids.

In recent years V-speciation studies have focused on the determination of V in natural waters, (Bosque-Sendra et al., 1998; Dupont et al., 1991; Miura, 1990; Yamane et al., 1998) biological systems (Elvingson et al., 1997; Hirayama et al., 1992; Kawakubo et al., 1995) and in industrial processes (De Beer and Coetzee, 1994; Murthy et al., 1989). A literature survey shows that most published analytical methods focus on the determination of total V or the determination of one species at a time. These methods include high performance liquid chromatography (De Beer and Coetzee, 1994; Komarova et al., 1991; Miura, 1990; Miura et al., 1990), spectrophotometry (Balaji et al., 1998; Bosque-Sendra et al., 1998; Chauhan and Kakkar, 1992; Iranpoor et al., 1992; Kawakubo et al., 1995; Murthy et al., 1989; Shah et al., 1991; Zucchi et al., 1998), flow injection (Grudpan and Nacapricha, 1991; Taylor et al., 1996; Yamane et al., 1998), atomic absorption spectrometery (Chakraborty and Das, 1994; Frankenberger et al., 1991; Yaman and Gucer, 1994), atomic emission spectrometery (Dupont et al., 1991; Hirayama et al., 1992), colorimetric (Serrat and Morell, 1994), and electrochemical methods (Ensafi and Naderi, 1997; Sander and Henze, 1996; Vukomanovic and Van Loon, 1994). Bosque-Serdra developed a method for V speciaton (Bosque-Sendra et al., 1998) based on the pre-concentration of V(IV) in the first step and V(V) after reduction with ascorbic acid in the second step. Only a few methods are reported for the simultaneous measurement of V species (Murthy et al., 1989; De Beer and Coetzee, 1994; Komarova et al., 1991). Disadvantages of these methods include: low sensitivities, interference and lengthy procedures.

No general accepted or standard method for the simultaneous determination of vanadium species is currently available. This is particularly true for industrial samples with complex matrices and environmental samples with low concentrations of V.

The aim of this work was to develop a simple, fast, cost-effective, and interference-free method for the simultaneous determination of V(IV) and V(V) that would be useful in a routine industrial or water quality laboratory. This was achieved by using a hyphenated technique approach with ion chromatography inductively coupled plasma optical emission spectrometry (IC-ICP-OES). V(IV) and V(V) species were complexed with EDTA, separated on an anion exchange column using a modified carbonate and bicarbonate buffer spiked with EDTA as eluant, and quantitatively and element-specifically determined by ICP-OES.

Experimental

Instrumentation

Ion chromatography

A Dionex ion chromatography pump (2000i) and Waters injection system in conjunction with a Dionex guard column were used as the separation system. Three different guard columns, AG4, AG5 and AG14 were evaluated in this work.

Table1 lists the optimised chromatographic conditions for separation of V(IV) and V(V).

TABLE 1
Optimised chromatographic conditions

Column	AG5 Guard Column
Eluant	12 mmol/ℓ $NaHCO_3$, 4 mmol/ℓ Na_2CO_3 and 20 mmol/ℓ EDTA
Flow rate	1.8 mℓ/min
Sample size	50 µℓ

* To whom all correspondence should be addressed.
☎(011) 489-2558; fax: (011) 4892819; e-mail: ppc@na.rau.ac.za
Received 20 November 2000; accepted in revised form 16 October 2001.

Inductively coupled plasma optical emission spectroscopy

A Varian Liberty 110 ICP-OES spectrometer was used as a detector in the chromatography system. ICP-OES conditions are summarised in Table 2. Ultrasonic nebulisation (Cetac, U-5000AT$^+$) was used to enhance detection limits.

TABLE 2
Optimised ICP-OES conditions for the detection of V

Plasma view height	8 mm
Search window	0.080 nm
Spectral order	1
PMT	650 V
Power	1.20 kW
Plasma gas flow rate	15.0 ℓ/min.
Auxiliary gas flow rate	1.50 ℓ/min.
Pump speed	25.0 rpm
Nebuliser pressure	150 KPa
Stabilisation time	15 s
Analytical line	309.311 nm

Reagents

The water used for the preparation of all solutions was produced with a Millipore deionising system composed of two mixed resins, an activated carbon filter and a diaphragm filter. This water had a resistivity of 18 MΩ.

- Ethylenediaminetetraacetic acid (disodium salt) (EDTA). SMM Chemicals (Pty) Limited. South Africa. 20 mmol/ℓ EDTA solution.
- Ammonium metavanadate (NH_4VO_3). Aldrich Chemical Company, Inc. USA. 1g/ℓ V(V) stock solution in 20 mmol/ℓ EDTA.
- V(IV) oxide sulphate ($VOSO_4.5H_2O$). Merck. Germany. 1g/ℓ V(IV) solution in 20 mmol/ℓ EDTA.
- Eluant stock solutions: A. 0.5 mol/ℓ Na_2CO_3 (anhydrous, BDH Chemical Ltd., England) in 20 mmol/ℓ EDTA; B. 0.5 mol/ℓ $NaHCO_3$ (Saarchem (Pty) Ltd., South Africa) in 20 mmol/ℓ EDTA.

Reagents were Analytical Reagent Grade. Standards and working eluents were prepared by appropriate dilution of the stock solutions with 20 mmol/ℓ EDTA. All solutions were filtered through a 0.22 micron membrane filter. All samples were treated with EDTA to keep the EDTA concentration at 20 mmol/ℓ, and then filtered.

Sample preparation

In the case of industrial samples, containing organic constituents which could damage the anion column such as Sasol Benfield-process samples analysed in this study, a simple chloroform extraction was used to remove organic components. This was done by extracting 10 mℓ of filtered sample with three 5 mℓ portions of chloroform.

Results and discussion

The stabilisation of V(IV)

The V^{4+} ion cannot exist in solution since the charge density is too large. Instead, the VO^{2+} ion is the dominant V(IV) species. The stability of the VO^{2+} ion depends on the prevailing conditions. In acidic solution and at low temperature, VO^{2+} can be kept for quite a long time. In alkaline solution, VO^{2+} species can be stored for about 4 d at room temperature. V(IV) is readily oxidised by oxygen in air in neutral or high pH media and the oxidation rate increases with increasing pH and temperature.

To prevent the oxidation of V(IV) species, a chelating ligand, such as EDTA, was chosen to complex it to form the V(IV)-EDTA anion complex, $[VO(EDTA)]^{2-}$ (Komarova, et al., 1991). This complex has been well characterised, and it is very stable with a stability constant of, logK =18.77 (Inczedy, 1976). No sign of oxidation was observed after keeping the V(IV)-EDTA complex for over six months at room temperature. V(V) can also form a complex with EDTA. The stability constant of the V(V)-EDTA complex (Inczedy, 1976) (log K=18.1) is almost the same as for the V(IV)-EDTA complex. When the V(IV)-EDTA complex is mixed with V(V) species, V(V) would compete with V(IV)-EDTA for EDTA. EDTA was also added to the V(V) stock solution. Thus, on mixing stock solutions to prepare samples containing both V(IV) and V(V), enough EDTA was present to stabilise both of the V complexes. The V(IV)-EDTA and the V(V)-EDTA complex, $[VO_2(EDTA)]^{3-}$ (Komarova, et al., 1991) are both anions, but they have different charges. The charge density properties of the two complexes form the basis for separating them on an anion exchange column. The V(IV)-EDTA complex elutes first, followed by the V(V)-EDTA complex.

Optimisation of experimental conditions

Column selection

Three Dionex anion exchange guard columns AG4, AG5, and AG14, were evaluated for the separation of V(IV) and V(V) EDTA complexes. Figure 1 shows the change in resolution as a function of eluant concentration for each column.

Note: The resolution, R, between two adjacent peaks in this paper was calculated by the following equation (He et al., 1996):

$$R = \frac{2\Delta t}{1.699(w_1 + w_2)}$$

where:

Δt is the difference in retention times of two adjacent peaks, and w_1 and w_2 are the half peak widths for two adjacent peaks.

The AG5 column showed the best resolution at all eluant strengths and was used in subsequent work.

Optimisation of the eluant

An eluant consisting of 2.8 mmol/ℓ Na_2CO_3 and 2.2 mmol/ℓ $NaHCO_3$ is recommended by the manufacturer as standard for the AG5 column. For this eluant, however, broad and irregular peaks were observed for the V species. Addition of EDTA, to ensure that the V-EDTA complexes remained stable during the elution process, resolved this problem. In addition, EDTA competes with the V-EDTA complexes for the exchange sites on the column, which increases the elution rate of the V-EDTA complexes, resulting in

TABLE 3
The optimisation of EDTA concentration
Column: AG5 guard column. Flow rate: 2.0 mℓ/min

EDTA Conc. (mmol/ℓ)	V(IV)			V(V)			Reso-lution
	R.T.* (min)	$W_{1/2}$ (min)	Peak Area	R.T. (min)	$W_{1/2}$ (min)	Peak Area	
5	0.386	0.0878	33 869	1.286	0.2333	30 263	3.30
10	0.330	0.0750	33 154	1.079	0.2150	32 264	3.04
15	0.334	0.0794	32 264	0.929	0.1861	30 096	2.64
20	0.307	0.0739	32 076	0.795	0.1589	30 888	2.47
25	0.317	0.0761	31 875	0.761	0.1522	30 410	2.29

* R.T. = retention time; $w_{1/2}$ = half peak width.

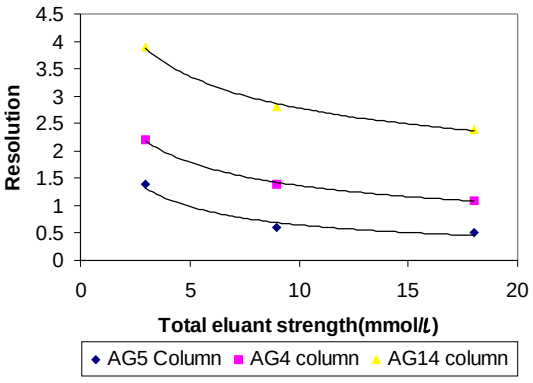

Figure 1
The change of resolution vs eluant concentration.
EDTA concentration in eluant: 20 mmol/ℓ, flow rate: 2.0mℓ/min.
Sample: A mixture of 10 mg/ℓ V(IV) and 10 mg/ℓ V(V)

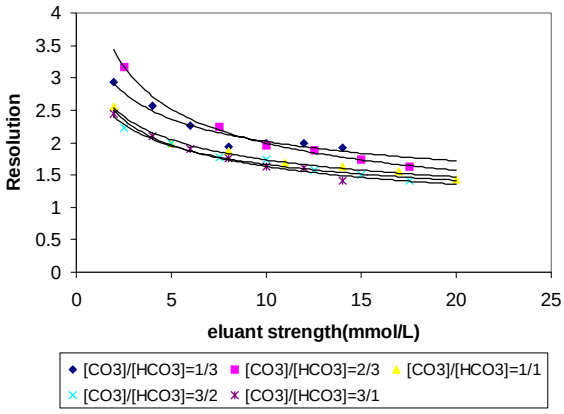

Figure 2
The change of resolution vs the eluant strength at different ratios of carbonate to bicarbonate in 20 mmol/ℓ EDTA.
Sample: 10 mg/ℓ V(IV) and 10 mg/ℓ V(V). Flow rate: 2.0 mℓ/min.
Column: AG5 guard column.

sharp and well-shaped peaks. Table 3 shows the results for the optimisation of the EDTA concentration.

The best resolution was obtained at lower EDTA concentrations, but the retention times were still too long (≥1 min.) for V(V), and the peaks were also very broad. At too high EDTA concentration, poor resolution resulted, especially for high concentration samples. 20 mmol/ℓ EDTA yielded a rapid separation with acceptable peak broadening. This EDTA concentration was used in all subsequent work.

The concentration of each eluant component can affect the retention time (shown in Fig. 1), half peak width, and measurement sensitivity (peak area). It was necessary to optimise the eluant strength (the total carbonate and bicarbonate concentration) and the ratio of carbonate to bicarbonate in the eluant. Figure 2 shows how the eluant strength influences the resolution for different ratios of carbonate to bicarbonate.

Although, good resolution was obtained at low eluant strength, retention times were long and, consequently, the peaks were broad, especially the V(V) peak. An intermediate eluant strength of 16 mmol/ℓ and a carbonate to bicarbonate ratio of 1 to 3 were chosen for further work. By using this eluant, the corresponding resolution was about 1.8. Higher eluant strength was unfavourable for the measurement of high concentration samples as poor resolution would be obtained.

Optimising flow rate

Table 4 shows the results which were obtained from the measurement of a sample containing 10 mg/ℓ V(IV) and 10 mg/ℓ V(V) in 20 mmol/ℓ EDTA at different eluant flow rates using the optimum eluant.

According to the Van-Deemter theory, flow rate does not have a significant effect on resolution for an anion-exchange column. The nearly constant resolution shown in Table 4 is consistent with the theory. High flow rate reduces analysis time, but also reduces sensitivity (small peak area). Low flow rate can increase sensitivity, but also increases analysis time. An intermediate flow rate of 1.8 mℓ/min was selected as a compromise between analysis time and sensitivity.

Optimising sample size

Different sample sizes were evaluated and experimental data are shown in Table 5.

The difference in retention times was negligible. Small sample size results in good separation but poor sensitivity, while large

TABLE 4
The effect of flow rate on the chromatographic separation of V(IV) and V(V) for the AG5 column

Flow rate mℓ/min	V(IV)			V(V)			Resolution
	R.T. (min)	$W_{1/2}$ (min)	Peak Area	R.T. (min)	$W_{1/2}$ (min)	Peak Area	
1.0	0.610	0.1600	38 396	1.630	0.3222	35 881	2.04
1.4	0.459	0.1094	34 883	1.177	0.2322	32 933	2.47
1.8	0.356	0.0861	32 887	0.908	0.1822	30 873	2.42
2.2	0.298	0.0717	29 532	0.743	0.1506	28 513	2.36
2.6	0.255	0.0550	26 566	0.617	0.1222	26 718	2.40
3.0	0.236	0.0544	24 720	0.563	0.1106	24 576	2.33

TABLE 5
The effect of sample size on the chromatographic separation of V(IV) and V(V). Sample: 10 mg/ℓ V(IV) and 10 mg/ℓ V(V). Flow rate: 1.8 mℓ/min

Sample size (µℓ)	V(IV)			V(V)			Resolution
	R.T. (min)	$W_{1/2}$ (min)	Peak Area	R.T. (min)	$W_{1/2}$ (min)	Peak Area	
30	0.349	0.0850	34 998	0.884	0.1861	31 467	2.32
40	0.335	0.0806	39 281	0.837	0.1978	38 302	2.04
50	0.364	0.0844	43 600	0.914	0.2150	42 281	2.16
60	0.364	0.0867	49 102	0.925	0.2278	48 904	2.10
70	0.371	0.0850	58 770	0.908	0.2222	56 351	2.06
80	0.367	0.0858	72 138	0.865	0.2250	70 572	1.89

sample size leads to good sensitivity but poor separation. For concentrated samples, too large a sample size can cause column overload. An intermediate sample size of 50 µℓ was used for all subsequent analyses.

Detection limits and analytical working ranges

Detection limits based on the average of the blank value plus three times its standard deviation, and analytical working ranges based on two times the best RSD of the calibration, were determined for the V species under the chromatographic conditions and ICP-OES conditions given in Tables 1 and 2. The detection limits of V(IV) species were 0.02 mg/ℓ and 2 µg/ℓ by using a glass nebuliser and ultrasonic nebuliser, respectively. For V(V) species, the detection limits were 0.05 mg/ℓ and 2 µg/ℓ by using the glass nebuliser and ultrasonic nebuliser, respectively. The analytical working ranges for V(IV) was 2.0 mg/ℓ to 366 mg/ℓ. The limits of quantitative determination for V(IV) were 2.0 mg/ℓ and 0.26 mg/ℓ by using a glass nebuliser and ultrasonic nebuliser, respectively. The limits of quantitative determination for V(V) were 4.1 mg/ℓ and 0.17 mg/ℓ by using the glass nebuliser and the ultrasonic nebuliser, respectively. The analytical working range for V(V) was 4.1 mg/ℓ to 310 mg/ℓ. Two problems were observed in measuring the V(V)-EDTA complex. The peak width increased with increasing concentration, while the retention time of the peak decreased. When using the AG5 guard column to analyse high concentration mixtures of V(IV) and V(V), poor resolution was obtained. In order to avoid peak overlap and to ensure good separation, a concentration range from 2 mg/ℓ to 100 mg/ℓ for V(IV) , and 10 mg/ℓ to 100 mg/ℓ for V(V) is recommended for routine analysis. For high concentration samples, appropriate dilution is necessary.

TABLE 6
The effect of the V(IV)/V(V) concentration ratio

	Ratio (R)	Result
V(IV)/V(V)	R<12	Quantitative results for V(IV) and V(V)
	12<R<20	Quantitative result for V(IV) and qualitative result for V(V)
	R>20	Only one peak for V(IV)
V(V)/V(IV)	R<10	Quantitative results for V(V) and V(IV)
	10<R<15	Quantitative result for V(V) and qualitative result for V(IV)
	R>15	Only one peak for V(V)

TABLE 7
Comparison of known concentrations with measured concentrations using the glass nebuliser. Correlation coefficient, R, for V(IV), was 0.9998, for V(V) it was 0.9982 (five standards calibration)

Sample No	V(IV)			V(V)			Reso-lution
	Known mg/ℓ	Measured mg/ℓ	Recovery	Known mg/ℓ	Measured mg/ℓ	Recovery	
1	2.0	1.9±0.2	95%	10.0	12.0±0.6	120%	1.7
2	5.0	4.6±0.5	92%	15.0	15.5±0.9	103%	1.5
3	20.0	19.6±1.2	98%	30.0	29.0±0.9	97%	1.2
4	50.0	51.6±1.1	103%	60.0	56.7±2.4	94%	1.0
5	100.0	99.3±3.1	99%	100.0	101.8±3.0	102%	0.7

TABLE 8
Comparison of known concentrations with measured concentrations for various V(IV) to V(V) ratios using the glass nebuliser. Correlation coefficient, R, for V(IV), was 0.9988, for V(V), it was 0.9997 (seven standards calibration)

Sample No	V(IV)			V(V)			Reso-lution
	Known mg/ℓ	Measured mg/ℓ	Recovery	Known mg/ℓ	Measured mg/ℓ	Recovery	
1	3.0*	3.8±0.6	127%	8.0	8.0±0.6	100%	1.7
2	100.0	102.9±2.0	103%	10.0	8.9±0.5	89%	0.9
3	80.0	76.7±2.1	96%	15.0	15.2±0.9	101%	1.4
4	40.0	39.2±1.1	98%	20.0	20.3±1.1	102%	1.3
5	40.0	38.2±2.0	97%	40.0	41.0±1.3	102%	1.1
6	20.0	19.6±1.4	98%	60.0	60.7±1.4	101%	0.9
7	10.0	9.8±0.8	98%	80.0	79.2±1.7	99%	0.8
8	8.0	8.7±1.9	109%	100.0	99.8±3.5	100%	0.8

* This concentration is near to the limit of quantitative determination for V(IV) at 2 mg/ℓ.

Interference study

The ratio of V(IV) and V(V)

When the concentration ratio of the two species is large, they interfere with each other during measurement. When the main species at high concentration is measured at reduced photomultiplier sensitivity, the detection of the other species at low concentration during the same measurement cycle is impaired. The results of the ratio study are shown in Table 6.

The reason why the ratio of V(IV)/V(V) is larger than the ratio of V(V)/V(IV) is that the V(IV) peak is narrower than the V(V) peak and it can be integrated more accurately than the V(V) peak.

Other elements and ions

At the chosen measurement wavelength of 309.311 nm, only the nearby Nb line at 309.418 nm can cause a spectral interference on the V measurement. Al concentrations higher than 100 mg/ℓ, can also interfere with V measurement, especially for V(V) measurement. This can be attributed to the fact that the Al emission line at 309.271 nm causes a background enhancement on the V-emission line. The common anions, such as: F^-, Cl^-, Br^-, CH_3COO^-, NO_2^-, NO_3^-, SO_4^{2-}, and HPO_4^{2-} do not cause interference.

Accuracy

The method was applied to samples with known concentrations of the V species. The results are shown in Tables 7 to 9. The confidence intervals were based on four replicate measurements and a confidence level of 95%.

A comparison of the known concentration with the measured concentration shows a good agreement. These results show that the method can be applied successfully to measure V species in water samples.

Effect of sample pH

Because the pH range could be expected to be large in industrial samples, the effect of sample pH on analytical results were investigated. Four self-prepared samples with the same concentration (20 mg/ℓ V(IV) and 20 mg/ℓ V(V)), but with different pH values, were analysed after adding 20 mmol/ℓ EDTA. The concentrations determined for the two species are summarised in Table 10. The results show no systematic variation as a result of pH variation. It proves that the method can be utilised to determine V species in samples which may have a large range of pH values, from pH 3.0 to pH 10.5.

TABLE 9
Comparison of known concentrations with measured concentrations for different ratios of V(IV) to V(V) using the ultrasonic nebuliser. Correlation coefficient, R, for V(IV), was 0.9993, and for V(V) , it was 0.9994 (seven standards calibration)

Sample No	V(IV)			V(V)			Reso-lution
	Known mg/ℓ	Measured mg/ℓ	Recovery	Known mg/ℓ	Measured mg/ℓ	Recovery	
1	0.2	0.13±0.06	65%	0.8	0.74±0.17	92%	1.2
2	0.6	0.65±0.02	108%	6.0	6.19±0.04	103%	1.1
3	1.0	1.00±0.08	100%	8.0	8.39±0.14	105%	0.8
4	2.0	2.02±0.09	101%	4.0	4.04±0.10	101%	1.1
5	3.0	2.96±0.08	99%	2.0	2.02±0.12	101%	1.2
6	4.0	4.11±0.24	103%	0.5	0.42±0.09	84%	1.5
7	5.0	4.92±0.78	98%	10.0	9.79±2.12	98%	1.2

TABLE 10
Effect of sample pH

Sample No.	pH	V(IV) concentration (mg/ℓ)		V(V) concentration (mg/ℓ)	
		Known	Measured	Known	Measured
1	10.2	20.0	20.9±0.3	20.0	20.5±0.5
2	8.9	20.0	20.0±0.4	20.0	19.7±0.4
3	7.0	20.0	20.6±0.7	20.0	20.3±0.7
4	3.6	20.0	20.8±0.5	20.0	20.0±0.4

TABLE 11
The preparation of simulated Sasol samples
Volume 2 mol/ℓ $(NH_4)_2S$ added/mℓ

Testing sample	Volume
Sample 1	0
Sample 2	2
Sample 3	4
Sample 4	6

TABLE 12
V(IV) and V(V) content of simulated Sasol samples. Reproducibility was based on three replicate determinations and a confidence level of 95%

Test sample	ICP	IC		
	Total V Conc. (mg/ℓ)	V(IV) (mg/ℓ)	V(V) (mg/ℓ)	Total V Conc. (mg/ℓ)
Sample 1	48.10±1.80	< Detection limit	49.10±1.59	49.58±1.59
Sample 2	47.88±1.27	76±0.47	43.25±2.17	49.01±2.64
Sample 3	47.63±1.42	13.68±1.89	36.52±2.54	50.20±4.43
Sample 4	47.13±0.78	21.06±0.92	28.27±1.20	50.33±2.12

The analysis of industrial samples

The method was evaluated by analysing eight samples obtained from different stages in the Benfield process for CO_2 removal used by the synthetic fuel manufacturer, Sasol. In this process the V(IV)/V(V) redox couple is used to protect the inner surfaces of steel pipes against corrosion.

The samples from Sasol were likely to contain two V species, V(V) and V(IV) in various ratios depending on the process phase. To simulate these different phases where different V(IV)/V(V) ratios would occur, a Benfield sample with an approximate concentration of 5 000 mg/ℓ V(V) buffered with 350 mmol/ℓ K_2CO_3 and 100 mmol/ℓ $KHCO_3$ at pH 10.5 was prepared. The sample was treated with different amounts of $(NH_4)_2S$ to reduce the V(V) to V(IV). This produced solutions with different V(IV)/V(V) ratios. $(NH_4)_2S$ was added to 0.5 mℓ sample which was then diluted to 50 mℓ in a volumetric flask with 20 mM EDTA. The volume of $(NH_4)_2S$ solution added is summarised in Table 11.

All test samples were filtered through 0.22 membrane filters and measured by direct ICP-OES to obtain the total V concentration and by the proposed IC-ICP-OES system to obtain the species concentration and the total V by summation. Table 12 summarises the results.

As expected, the V(IV) content increased with increasing amounts of reducing agent. The total V content obtained by the two methods was comparable, with the IC-ICP-OES results somewhat closer to the expected 50 mg/ℓ. This suggests that the proposed method will give accurate results in the measurement of industrial effluent and industrial process samples.

Chloroform extraction

Since the Sasol samples could contain organic constituents which could damage the anion column, a simple chloroform extraction was used to remove the organic components. To determine whether

this extraction can cause loss of V or not, the samples obtained from Sasol were analysed for total V content by ICP-OES before and after extraction. The pH value of the samples was about 11. Test samples were prepared by 100-fold dilution with deionised water in a 50 mℓ volumetric flask. 3.0 mℓ 65% HNO_3 was added to the flask to adjust the test sample's pH value to that of the standards. The total V concentration in 3 of the 8 Sasol samples was also determined by an independent analytical laboratory, Modderfontein Laboratory Services(MLS) in Johannesburg by ICP-OES. The three samples were prepared as follows: 0.5 mℓ of raw sample was diluted with 50 mℓ deionised water acidified with 7.52 mℓ 65% HNO_3, then heated for 20 min in a water bath at 60°C, filtered through a 0.22 micron membrane filter, transferred to a 100 mℓ volumetric flask and made up to the mark with deionised water. The total V concentration before and after extraction and the results obtained from MLS after correction for dilution are compared in Table 13.

Statistical analysis shows no difference between the results before and after extraction, and the MLS measurements show good agreement with the results obtained in this work. Consequently, all test samples prepared for the IC-ICP-OES system were diluted 100-fold with 20 mmol/ℓ EDTA after triple extraction with chloroform. No nitric acid was added, because the pH values of prepared Sasol samples were between 8~9, within the working pH range for the proposed method. Double filtration through 0.22 micron membrane filters was performed to prevent the column from blocking. To evaluate possible matrix effects caused by complex Benfield samples, test samples were determined by the standard addition method. The results are summarised in Table 14.

Agreement between the total V concentrations shown in Table 13 and the sum of the speciation results shown in Table 14 is excellent.

TABLE 13
The comparison of total vanadium concentration (mg/ℓ)

Sample No.	Before extraction 100-fold dilution	After extraction 100-fold dilution	MLS measurement 100-fold dilution
1	51.23	50.74	
2	52.16	50.84	
3	62.05	63.06	68
4	71.08	69.38	
5	70.11	71.28	68
6	42.30	43.37	44
7	61.32	61.16	
8	65.08	64.14	

Conclusion

The proposed IC-ICP-OES system offers an accurate, precise and interference-free method for the simultaneous determination of V(IV) and V(V) in industrial and water samples. The method is fast (less than one minute per run), simple and relatively inexpensive since it utilises a guard column instead of an expensive analytical column.

The following should, however, be kept in mind:

- At high concentration levels, Al broaden the V(V) peak, because its emission line (309.271 nm) is close to the V emission line at 309.311 nm. Proper dilution of samples may solve this problem.
- With high concentration of V in samples, good baseline resolution can be achieved by using a AG5 guard column coupled with AS5 analytical column, or the AG5 column only can be used after proper dilution.
- At low V concentrations, an ultrasonic nebuliser is recommended instead of a glass nebuliser.

Acknowledgements

The authors thank the NRF for financial support, and Sasol for providing test samples.

TABLE 14
Comparison of V concentrations in Benfield samples determined using external standards and the standard addition method. Number of replicate determinations is 3.

Test sample No.	External standards			Standard addition		
	V(IV) (mg/ℓ)	V(V) (mg/ℓ)	Total (mg/ℓ)	V(IV) (mg/ℓ)	V(V) (mg/ℓ)	Total (mg/ℓ)
1	16.18±0.46	36.35±0.05	52.53±0.52			
2**	Undetectable	49.42±0.12	49.42±0.12			
3**	Undetectable	64.78±1.94	64.78±1.94	1.84*	64.04	64.04
4	18.67±2.28	51.84±1.91	70.51±4.19	18.76	53.64	72.40
5	18.32±1.46	48.80±2.18	67.12±3.64	20.24	52.78	73.02
6**	Undetectable	41.40 ±1.59	41.40±1.59	1.74*	48.08	48.08
7	17.24±1.76	44.48±3.05	61.72±4.81			
8	18.12±2.93	41.51±1.94	59.63±4.87			

* Values below limit of quantitative detection
** The sample was obtained after the oxidation process used to convert V(IV) to V(V)

References

BALAJI BK, SARAVANAKUMAR G, MURUGESAN P and MISHRA G (1998) A modified catalytic-photometric method for the determination of vanadium in chloride rich hydro-geochemical samples. *Talanta* **46** 1299.

BOSQUE-SENDRA JM, VALENCIA MC and BOUDRA S (1998) Speciation of vanadium(IV) and vanadium(V) with Eriochrome Cyanine R in natural waters by solid phase spectrophotometry. *Fresenius' J. Anal. Chem.* **360** 31.

BROWNING EMD (1961) *Toxicity of Industrial Metal*. Publishing Co., Butterworth, Great Britain.

CHAKRABORTY R and DAS AK (1994) Determination of vanadium by ETAAS using chromium nitrate as chemical modifier. *Fresenius' J. Anal. Chem.* **349** 774.

CHAUHAN RS and KAKKAR LR (1992) Extractive separation and photometric determination of vanadium with Benzoylacetone. *Bull. Chem. Soc. Japan* **65** 1033.

COTTON FA and WILKINSON G (1988) *Advanced Inorganic Chemistry* (5th edn.) Publishing Co., Wilner, New York, USA.

DE BEER H and COETZEE PP (1994) Vanadium speciation by ion chromatography. *Fresenius' J. Anal. Chem.* **348** 806.

DUPONT V, AUGER Y, JEANDEL C and WARTEL M (1991) Determination of vanadium in seawater by inductively coupled plasma atomic emission spectrometry using chelating resin column preconcentration. *Anal. Chem.* **63** 520.

ELVINGSON K, CRANS DC and PETTERSSON L (1997) Speciation in vanadium bioinorganic system. 4. Interactions between vanadate, adenosine, and imidazole – An aqueous potentiometric and ^{51}V NMR study. *J. Am. Chem. Soc.* **119** 7005.

ENSAFI AA and NADERI B (1997) Catalytic determination of ultra trace amounts of vanadium with detection by linear sweep voltammetry. *Fresenius' J. Anal. Chem.* **358** 480.

FRANKENBERGER A, BROOKS RR and HOASHI M (1991) Determination of vanadium in steels and geological materials by liquid-liquid extraction and graphite furnace atomic absorption spectrometry. *Anal. Chim. Acta*. **246** 359.

GRUDPAN K and NACAPRICHA D (1991) Flow-injection radiorelease analysis for vanadium. *Anal. Chim. Acta*. **246** 329.

HE XL, ZHAO SZ and WU SH (1996) *Analytical Chemistry*. Beijing, P.R. China.

HIRAYAMA K, KAGEYAMA S and UNOHARA N (1992) Mutual separation and preconcentration of vanadium(V) and vanadium(IV) in natural waters with chelating functional group immobilized silica gels followed by determination of vanadium by inductively coupled plasma atomic emission spectrometry. *Analyst.* **117** 13.

INCZEDY J (1976) *Analytical Applications of Complex Equilibria*. Publishing Co., Ellis Horwood, United Kingdom.

IRANPOOR N, MALEKI N, RAZI S and SAFAVI A (1992) Spectrophotometric determination of vanadium in different oxidation states with pyrogallol. *Talanta* **39** (3) 281.

KAWAKUBO S, OGIHARA K and IWATSUKI M (1995) Catalytic spectrofluorimetric determination of vanadium using oxidation of o-phenylenediamine with bromate in the presence of gallic acid. *Analyst.* **120** 2719.

KOMAROVA TV, OBREZKOV ON and SHPIGUN OA (1991) Ion chromatographic behaviour of anionic EDTA complexes of vanadium(IV) and vanadium(V). *Anal. Chim. Acta* **254** 61.

MIURA J (1990) Determination of trace amounts of vanadium in natural waters and coal fly ash with 2-(8-quinolylazo)-5-(demethylamino)phenol by reversed-phase liquid chromatography-spectrophotometry. *Anal. Chem.* **62** 1424.

MIURA J, HOSHINO H and YOTSUYANAGI T (1990) Determination of trace amounts of vanadium in air samples with 2-(8-quinolylazo)-5-N,N-diethylaminophenol by reversed-phase liquid chromatography. *Anal. Chim. Acta*. **233** 121.

MURTHY GVR, REDDY TS and RAO SB (1989) Extraction and simultaneous spectrophotometric determination of vanadium(IV) and vanadium(V) in admixture with 2-hydroxyacetophenone oxine. *Analyst.* **114** 493.

SANDER S and HENZE G (1996) Adsorptive stripping voltammetric determination of vanadium as chloranilic acid complex. *Fresenius' J. Anal. Chem.* **356** 259.

SERRAT FB and MORELL GB (1994) Colorimetric method for the determination of vanadium with tannic acid in water and oils. *Fresenius' J. Anal. Chem.* **349** 717.

SHAH N, DESAI MN, MENON SK and AGRAWAL YK (1991) Ion-exchange separation and spectrophotometric determination of vanadium in environmental samples. *Talanta* **38** (6) 649.

TAYLOR MJC, MARSHALL GD, WILLIAMS SJS, VAN STADEN JF and SALING C (1996) The determination of vanadium(V) in the presence of vanadium(IV) using 4-(2-pyridylazo)resorcinol in a flow-injection manifold. *Anal. Chim. Acta* **329** (3) 275.

VUKOMANOVIC DV and VANLOON GW (1994) Voltammetric determination of vanadium with adsorptive preconcentration of the pyrocatechol violet complex. *Talanta* **41** (3) 387.

YAMANE T, OSADA Y and SUZUKI M (1998) Continuous flow system for the determination of trace vanadium in natural waters utilizing in-line preconcentration/separation coupled with catalytic photometric detection. *Talanta* **45** 583.

YAMAN M and GUCER S (1994) Determination of vanadium in biological matrices by flame atomic absorption spectrometry with activated carbon enrichment. *Fresenius' J. Anal. Chem.* **350** 504.

ZUCCHI C, FORNERIS M, MARTINEZ L, OISINA R and MARCHEVSKY E (1998) Sensitive spectrophotometric determination of vanadium with hydrogen peroxide and 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol after extraction with N-benzoyl-N-phenylhydroxylamine. *Fresenius' J. Anal. Chem.* **360** 128.