

CHAPTER 9

MEASUREMENT OF VANADIUM

9.1 WAVELENGTHS SELECTED

No references to the measurement of vanadium in tungsten carbide by ICP-OES could be found in the literature, although a standard method for the analysis of vanadium in tungsten carbide, using atomic absorption spectrometry by the method of standard additions (ISO, 1983), exists.

There are several lines which are recommended for vanadium analysis, the most commonly used being 268.796 nm, 270.094 nm (Jobin Yvon, version 5 software), 292.402 nm, 309.311 nm, 310.230 nm and 311.071 nm (Thompson & Walsh, 1983). All these lines were investigated by comparing the emission profiles of solutions of vanadium in acid with those of vanadium in tungsten and vanadium in cobalt. The vanadium emission lines at 292.402 nm and 311.071 nm were found suitable for analytical purposes.

Another vanadium emission line at 290.88 nm was recommended by Thompson & Walsh (1983) for the measurement of vanadium in soils. Since there are three tungsten emission lines at 290.840 nm, 290.849 nm and 290.912 nm (Harrison, 1969) which may interfere when vanadium in tungsten carbide is measured, this line was not evaluated.

9.2 MATRIX EFFECTS AND INTERFERENCES

Cobalt was found to cause no interferences at the 268.796 nm vanadium emission line. The emission profiles of vanadium in 0.5 M hydrochloric acid and vanadium in a cobalt solution are compared in Figure 9.1.

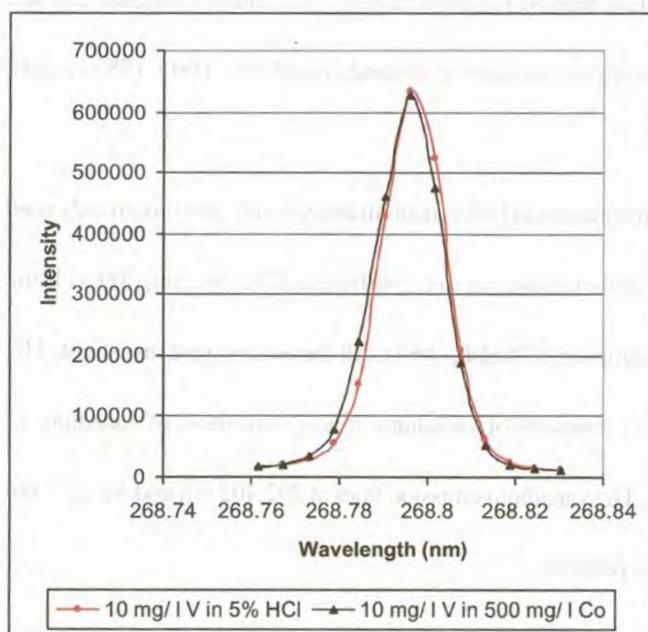


Figure 9.1: Effect of Co on V at 268.796 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

However, the tungsten emission lines at 268.800 nm and 268.822 nm (Harrison, 1969) were found to interfere slightly with quantitative vanadium analysis at 268.796 nm, as can be observed in Figure 9.2.

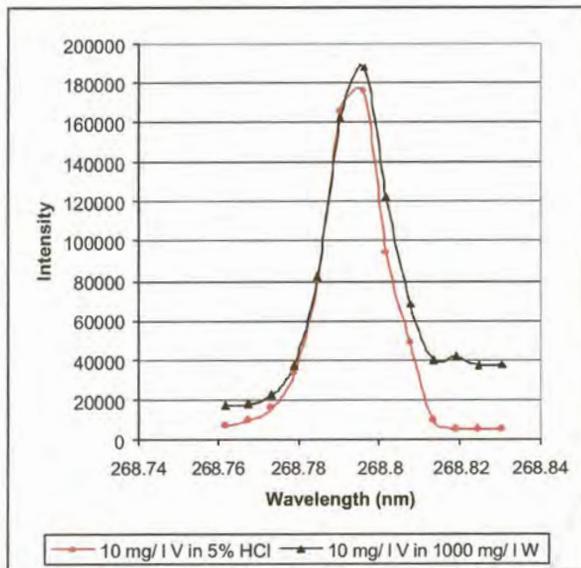


Figure 9.2: Effect of *W* on *V* at 268.796 nm (JY-24 ICP-OES),
where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

The 270.094 nm vanadium emission line was tested with vanadium in cobalt and tungsten matrices. Although the results in Figure 9.3 seem to show an interference by cobalt, it was found through measurements of solutions of the certified reference material (NBS 889) that no significant interferences from cobalt at the 500 mg/ℓ level occurred.

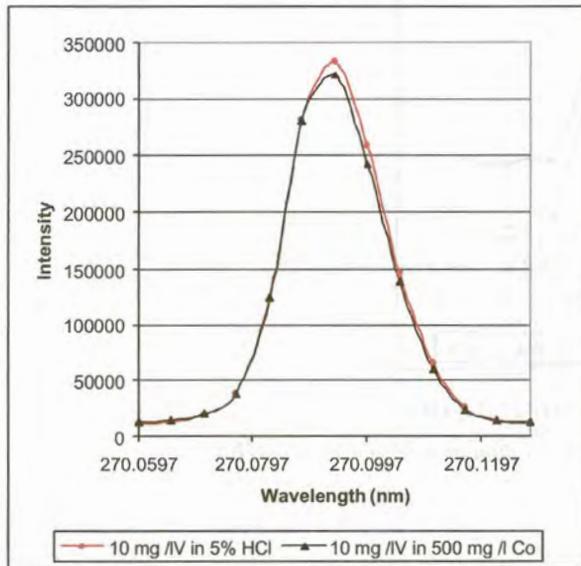


Figure 9.3: Effect of Co on V at 270.094 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

A tungsten emission line is cited in the literature at 270.106 nm (Harrison, 1969). From Figure 9.4, it can be seen that this does indeed interfere with the measurement of vanadium at 270.094 nm.

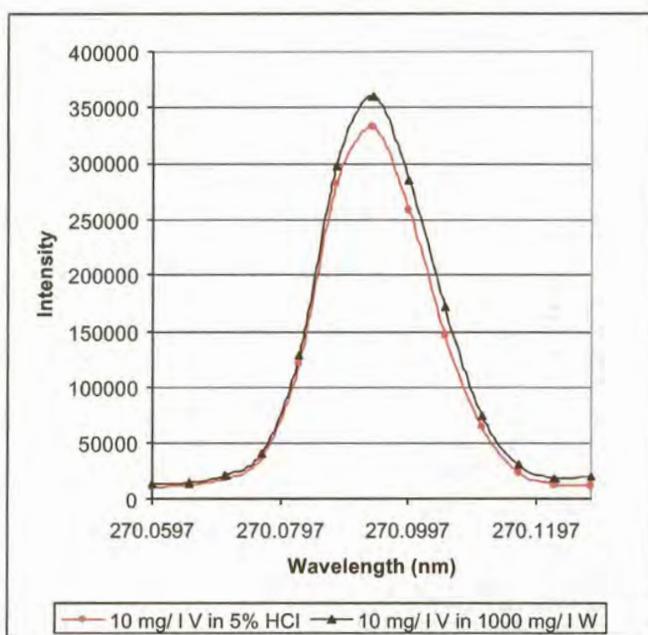


Figure 9.4: Effect of W on V at 270.106 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

There is a tungsten emission line at 292.354 nm (Boumans, 1984; Harrison, 1969) but this is not close enough to the vanadium emission line at 292.402 nm to influence the measurements. Tungsten at the 1000 mg/ℓ level was confirmed to have very little effect on vanadium analyses at 292.402 nm (Figure 9.5).

The presence of cobalt in the solutions was not found to affect the quantitative results at 292.402 nm, as can be seen in Figure 9.6. No cobalt emission lines are reported by either Boumans (1984) or Harrison (1969) near this wavelength.

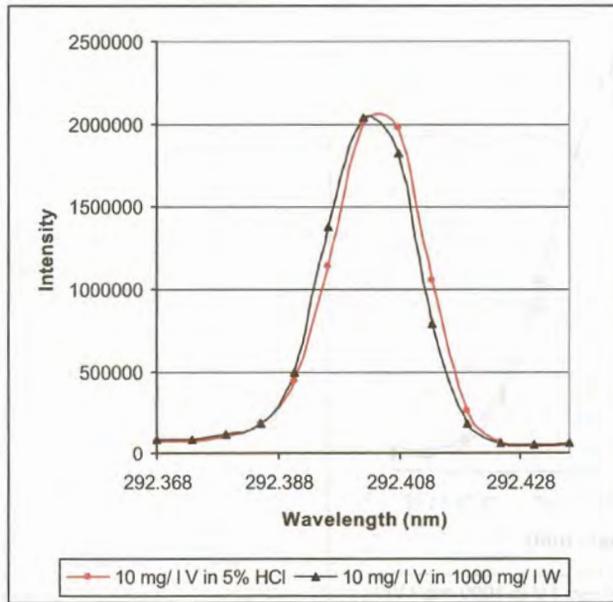


Figure 9.5: Effect of W on V at 292.402 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

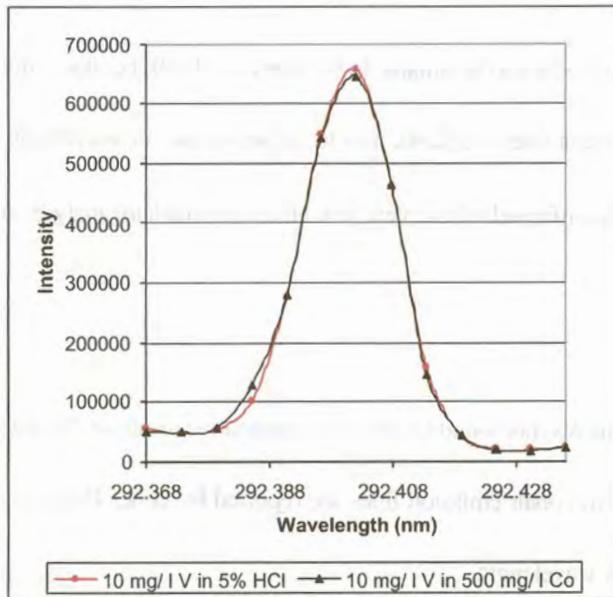


Figure 9.6: Effect of Co on V at 292.402 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

The 309.350 nm tungsten emission line (Boumans, 1984; Harrison, 1969) was found to interfere with quantitative vanadium analysis at 309.311 nm but this line could be used to confirm the approximate vanadium concentration in the sample solution.

A baseline shift was observed at the line 310.230 nm when vanadium solutions with an acid matrix were compared to solutions with a tungsten carbide-cobalt matrix. This was thought to be due to a tungsten emission line at 310.222 nm (Harrison, 1969).

The 311.071 nm vanadium emission line was found not to be subject to tungsten interference (Figure 9.7). Boumans (1984) and Harrison (1969) report a tungsten emission line at 311.112 nm but this was found not to have an influence on the vanadium measurements.

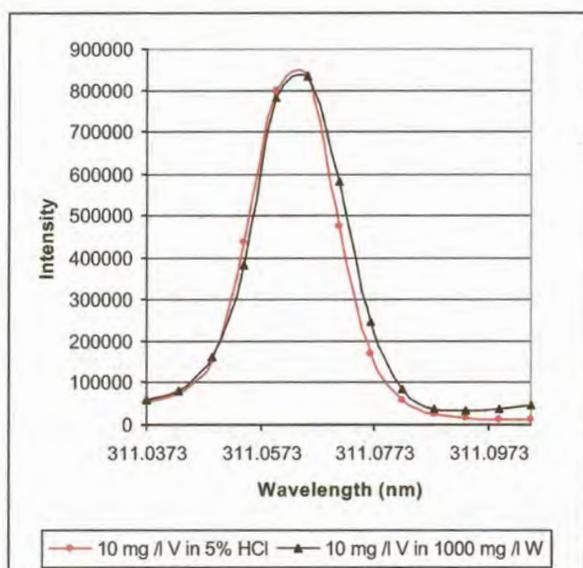


Figure 9.7: Effect of W on V at 311.071 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

A cobalt emission line is reported by Harrison (1969) at 311.083 nm but it is not mentioned by

Boumans (1984). On comparing the emission profiles of solutions of vanadium in 0.5 M hydrochloric acid and in 500 mg/ℓ cobalt solution (Figure 9.8) no significant effect could be observed.

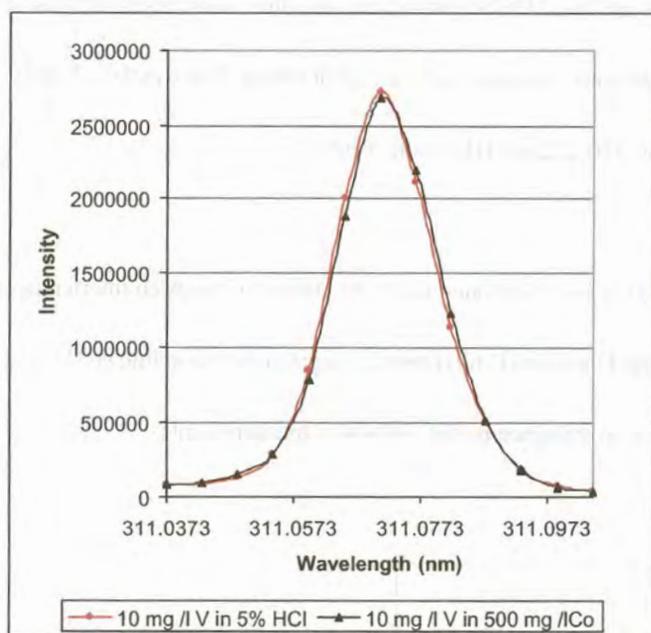


Figure 9.8: Effect of Co on V at 311.071 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

To be certain that the effect of cobalt and tungsten on the measurement of vanadium at 311.071 nm had been correctly assessed, an aliquot of a cemented carbide reference material, NBS 889, which contained no vanadium, was dissolved in hydrogen peroxide/ aqua regia. Vanadium was added (spiked) to a portion of this solution at the 10 mg/ℓ level. The emission profile of the spiked solution was compared to that of 10 mg/ℓ vanadium in 0.5 M hydrochloric acid. From Figure 9.9, it is clear that there is no significant interference from tungsten or cobalt on vanadium measurements at 311.071 nm. At a dilution factor of 1000, the solution of NBS 889 contained about 95 mg/ℓ cobalt and about 700 mg/ℓ tungsten, as well as approximately 46 mg/ℓ tantalum

and approximately 40 mg/ℓ titanium. The experiment thus confirms that tantalum and titanium at these levels do not interfere with the vanadium measurement either.

A similar result was obtained when the experiment was repeated at 292.402 nm.

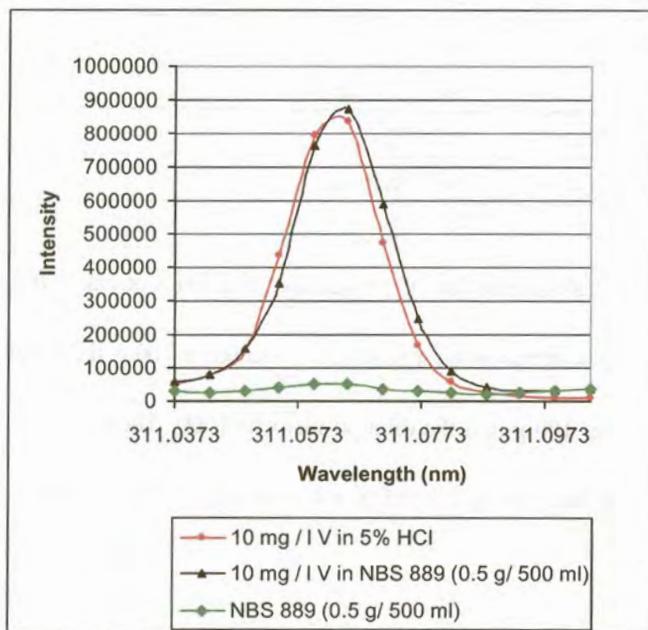


Figure 9.9: The effect of the matrix of an actual tungsten carbide sample on the measurement of V at 311.071 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

9.3 CALIBRATION SOLUTIONS

The samples analysed contained vanadium in concentrations ranging from 0 to 8 g/ 100 g. In most of the samples, the vanadium concentration was in the region of 0.6 g/ 100 g. It was found convenient to dilute 0.5 g sample to 500 ml to give a vanadium concentration of in the measurement solution of about 6 mg/ℓ.

Table 9.1 gives a summary of a typical composition of the analytical solution with respect to

vanadium, cobalt and tungsten.

Table 9.1: Summary of analytical solution composition during the analysis of vanadium in tungsten carbide

Analyte	Vanadium
Mass dissolved	0.5 g
Final volume	500 ml
Dilution factor	1000
Concentration vanadium in solution	0 – 80 mg/ ℓ
Concentration cobalt in solution	10 – 150 mg/ ℓ
Concentration tungsten in solution	~ 850 mg/ ℓ
Matrix matching of calibration solutions?	Not required

Table 9.2 gives a summary of a typical scheme for the preparation of a series of calibration solutions if the expected vanadium concentration in the sample is about 0.6 g/ 100 g, the cobalt content in the sample is about 9.6 g/ 100 g and the dilution factor is 1000. The vanadium solution was obtained from Merck Chemicals as a certified solution with a concentration of 1000 mg/ ℓ.

Table 9.2: Preparation of vanadium calibration reference solutions: sample vanadium concentration 0.6 g/ 100 g and cobalt concentration 9.6 g/ 100 g

V concentration required (mg/ ℓ)	Concentration of V stock solution (mg/ ℓ)	Volume of V stock solution (ml)	Volume of 32% HCl (ml)	Final volume (ml)
0	-	-	5	100.00
1	25	4.00	5	100.00
5	1000	0.50	5	100.00
10	1000	1.00	5	100.00

A four point calibration of the JY-24 ICP-OES was performed at 292.402 nm and at 311.071 nm. The calibration curve at 292.402 nm can be viewed in Appendix 4, Figure A7. A coefficient of correlation (r^2) of 1.0000 was obtained. The limit of detection (LOD), calculated from this

data according to the principles of Miller & Miller (1993), was 0.03 mg/ ℓ and the limit of quantification (LOQ) 0.1 mg/ ℓ.

At 311.071 nm, the coefficient of correlation (r^2) was found to be 0.9999, the LOD 0.1 mg/ ℓ and the LOQ 0.5 mg/ ℓ (Appendix 4, Figure A8).

When tungsten carbide samples with concentrations of vanadium above 0.7 g/ 100 g were analysed, the sample solutions were diluted so that the vanadium concentration in the solutions fell approximately in the middle of the calibration range. Sometimes the vanadium calibration range was extended to 50 mg/ ℓ. The usual linearity checks were performed and limit of quantitation calculated before sample measurements were made.

9.4 REFERENCE MATERIALS AND QUALITY CONTROL

Several checks were done to ensure valid results:

- i) The certified reference material of cemented carbide, NBS 889 (obtained from NIST, USA), which was used for quality control with cobalt, tantalum and titanium contained no vanadium. A solution of this cemented carbide was spiked with vanadium to check the measurement procedure. Solutions of vanadium in different matrices (0.5 M hydrochloric acid, 60 mg/ ℓ cobalt, and 1000 mg/ ℓ tungsten) were also measured.
- ii) A certified tungsten carbide reference material which contains vanadium was not available. However, a sample of tungsten carbide which had been analysed by the Boart Longyear Research Centre by XRF was obtained.

- iii) The vanadium concentration in a commercial sample was measured using the external calibration procedure described in Section 9.3. It was then also analysed by the method of standard additions and the results compared.

An aliquot of vanadium-free cemented carbide, NBS 889, was dissolved by the hydrogen peroxide/ aqua regia method described in Section 4.3. Aliquots of this solution were spiked with vanadium to give final vanadium concentrations of 5 mg/ℓ and 10 mg/ℓ, respectively. The final solution had a dilution factor of 1000 and thus a cobalt concentration of about 96 mg/ℓ. A series of vanadium calibration solutions, similar to those in Table 9.2, were prepared and the JY-24 ICP-OES calibrated with these solutions at 292.402 nm and 309.311 nm. The spiked solutions of the cemented carbide were then measured. Solutions of 5 mg/ℓ vanadium in respectively, 0.5 M hydrochloric acid, 60 mg/ℓ cobalt and 1000 mg/ℓ tungsten, were also measured.

The measurements were repeated after the instrument had been calibrated with vanadium solutions in 60 mg/ℓ cobalt. The results for the measurements after calibration with vanadium in hydrochloric acid are tabulated in Table 9.3.

Table 9.3: Analysis of solutions of cemented carbide, NBS 889, spiked with vanadium

Spiked concentration (mg/ℓ)	Measured concentration (mg/ℓ) at	
	292.402 nm	309.311 nm
5	4.950	4.849
	4.881	4.827
10	9.901	9.698
	9.872	9.654

The results in Table 9.3 show that measurement results within 5% of the expected concentrations can be obtained at 292.402 nm and 309.311 nm without matrix matching of the reference solutions. The results of the measurement of the vanadium solutions in the different matrices were all within 5% of the prepared concentrations. For a 5 mg/ℓ solution of vanadium this would be a range of 4.75 to 5.25 mg/ℓ, and for the 10 mg/ℓ solution, a range of 9.5 to 10.5 mg/ℓ. The results obtained after the instrument was calibrated with vanadium solutions in 60 mg/ℓ cobalt also fell within this range. It was concluded that the accuracy of the vanadium measurements at 292.402 nm or 311.071 nm were not affected by cobalt, tungsten, tantalum or titanium.

The vanadium concentration in the sample which had been analysed by Boart Longyear Research Centre by XRF, was given as 0.63 g/ 100 g. This sample was dissolved a number of times by the hydrogen peroxide/ aqua regia method and the vanadium concentration measured by ICP-OES at 292.402 nm and 311.071 nm. The results are tabulated in Table 9.4.

Table 9.4: ICP-OES vanadium measurement results for a tungsten carbide sample previously measured by XRF

Aliquot number	Vanadium measurement results (g/ 100 g) at	
	292.402 nm	311.071 nm
1	0.578	0.576
2	0.586	0.571
3	0.595	0.572
4	0.574	0.573
5	0.590	0.576
6	0.578	0.573

When the results in Table 9.4 were analysed by a two factor ANOVA test using Microsoft Excel, there was no significant difference in the precision between the results obtained at the two wavelengths. There was a slight statistical difference in the accuracy of the results for the two

different wavelengths, the mean concentration being 0.58 g/ 100 g at 292.402 nm and 0.57 g/ 100 g at 311.071 nm. In Table 9.3 all the results of the spiked solutions fall within 5% of the prepared value, although the results at 311.071 nm are slightly lower than those at 292.402 nm. Whether the results at the two wavelengths differ significantly is not conclusive, and thus the average of the results for both wavelengths were used when commercial samples were analysed. The procedure of Miller & Miller (1993), using the formula:

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}, \quad \text{where } t_{(0.05;13)} = 2.160, s = 0.0071 \text{ and } n = 14$$

produces a concentration of 0.58 ± 0.01 g/ 100 g. All the values obtained in Table 9.4, except 0.595, fall within this range. The sample was used as a secondary reference material with commercial samples.

The vanadium concentration in a commercial sample was measured using the external calibration procedure described in Section 9.3 at the 292.402 nm vanadium emission line. An average vanadium concentration of 0.602 g/ 100 g was obtained. The sample solution was then divided into 6 portions and increasing concentrations of vanadium added to each portion. The added vanadium concentrations ranged from 0 to 10 mg/ ℓ. These solutions were then analysed at 292.402 nm by the method of standard additions. The results are tabulated in Table 9.5. By the method of standard additions, a result of 0.599 g/ 100 g was achieved. This is very close to the result for the external calibration method, which was 0.602 g/ 100 g.

Table 9.5: Results of ICP-OES analysis by the method of standard additions

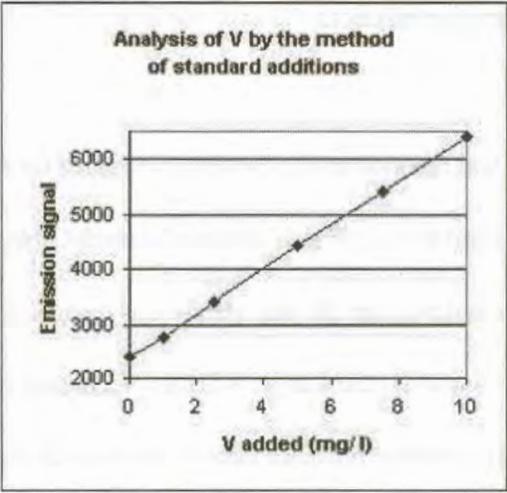
Vanadium added (mg/ℓ)	Signal (292.402 nm)
0	2380
1	2762
2.5	3422
5	4447
7.5	5418
10	6416

Regression Statistics	
Multiple R	0.999873355
R Square	0.999746725
Adjusted R Square	0.999683406
Standard Error	28.04282929
Observations	6

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	12416567	12416567	15789.12	2.41E-08
Residual	4	3145.601	786.4003		
Total	5	12419713			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	2387.385714	18.04978	132.2668	1.96E-08	2337.271	2437.5
X Variable 1	404.6417582	3.220266	125.6548	2.41E-08	395.7008	413.5827

Concentration V in soln =	a/b =	5.900mg/ℓ
Sample mass		0.4928 g
Sample volume		500 ml
Dilution factor		1014.61
Sample V concentration =		0.599g/ 100 g



9.5 DISCUSSION AND CONCLUSIONS

From the results of the spiking experiments, it can be concluded that accurate vanadium measurements can be made at 292.402 nm and 311.071 nm without matrix matching of the reference solutions. One of the samples was analysed by both the external calibration method and the method of standard additions at 292.402 nm. The results were very similar (0.602 and

0.599 g/ 100 g, respectively), confirming that the matrix did not contribute significantly to measurement errors.

As was reported earlier, the results obtained for the multiple ICP-OES analysis of the sample obtained from the Boart Longyear Research Centre, were significantly lower than the XRF result reported by them. No uncertainty was reported for the result of 0.63 g/ 100 g. On enquiry, it was found that the sample was part of a routine XRF analytical run. It was only analysed once and no certified reference material was used during the analysis. The results found by the Boart Longyear Research Centre were suitable for their particular research application and fell within their expected range. The average result for the ICP-OES analysis was 0.58 ± 0.01 g/ 100 g. There is no evidence that the ICP-OES measurement procedure did not give accurate results. Townshend et al (1995, p5098, p5364) suggest that nitric and hydrofluoric acid can be used to dissolve both tantalum and vanadium. Since tantalum in tungsten carbide was successfully analysed by the same dissolution procedure and measurement technique, there is no evidence that vanadium cannot be completely dissolved by the hydrogen peroxide/ aqua regia method.

In some cases, no vanadium could be detected in the samples at a dilution factor of 1000. The 0.5g/ 100 ml solutions were then measured by ICP-OES at the vanadium emission lines. From the calibration data at 292.402 nm, a vanadium detection limit (LOD) of 0.001 g/ 100 g and a limit of quantification (LOQ) of 0.002 g/ 100 g in the sample was therefore possible. The calculations were performed according to the guidelines of Miller & Miller (1993).

No significant effect from tungsten, cobalt, titanium and tantalum on the measurement of vanadium was observed at the levels found in commercial samples, but it has been found that additional elements may be introduced into tungsten carbide in a research environment. The effects of these elements had not been tested and it was therefore considered prudent to measure the vanadium concentration at two different analytical wavelengths. The effect of a certain element on the measurement of an analyte element is not likely to be exactly the same at two different emission wavelengths. A discrepancy between the results at two wavelengths would be cause for an investigation and the reporting of erroneous results could be prevented.

Although no certified reference material was available for analysis, it can be concluded from the validation methods investigated that vanadium in tungsten carbide can be accurately determined using the hydrogen peroxide/ aqua regia dissolution procedure together with the ICP-OES measurement technique.