CHAPTER 7

MEASUREMENT OF TANTALUM

7.1 WAVELENGTHS SELECTED

Lines recommended in the literature for the ICP-OES analysis of tantalum are 226.230 nm, 233.198 nm, 240.063 nm, 263.558 nm and 268.517 nm (Thompson & Walsh, 1983). Piippanen et al (1997a) used the 296.513 nm line for the analysis of tantalum in tungsten carbide.

On testing the 226.230 nm, 233.198 nm, 240.063 nm, 263.558 nm and 268.517 nm lines for suitability of use with the tungsten carbide matrix, the 240.063 nm and 268.517 nm lines were finally selected for quantitative work. None of the lines were found to be free of interference from high concentrations of tungsten; only the degree of interference differed. Positive results were initially obtained for samples which contained no tantalum because of the effect of tungsten, which is present in relatively high concentrations in all the samples. These results were rejected upon further investigation.

7.2 INVESTIGATION OF MATRIX EFFECTS AND INTERFERENCES

To study the interference effects of cobalt and tungsten on the measurement of tantalum, mixtures of 10 mg/ ℓ tantalum in the following matrices were prepared:

i) deionised water

ii) 500 mg/ ℓ cobalt

iii) 1000 mg/ ℓ tungsten.

According to Boumans (1984) and Harrison (1969), a tungsten emission line occurs at 226.232 nm, which is very close to the tantalum emission line at 226.230 nm. A profile of 10 mg/ ℓ tantalum in 0.5 M hydrochloric acid was compared with that of the same concentration of tantalum in 1000 mg/ ℓ tungsten. In Figure 7.1 it can be seen that 1000 mg/ ℓ tungsten has the effect of apparently enhancing the tantalum signal at 226.230 nm. This is more probably interfering emission from tungsten.

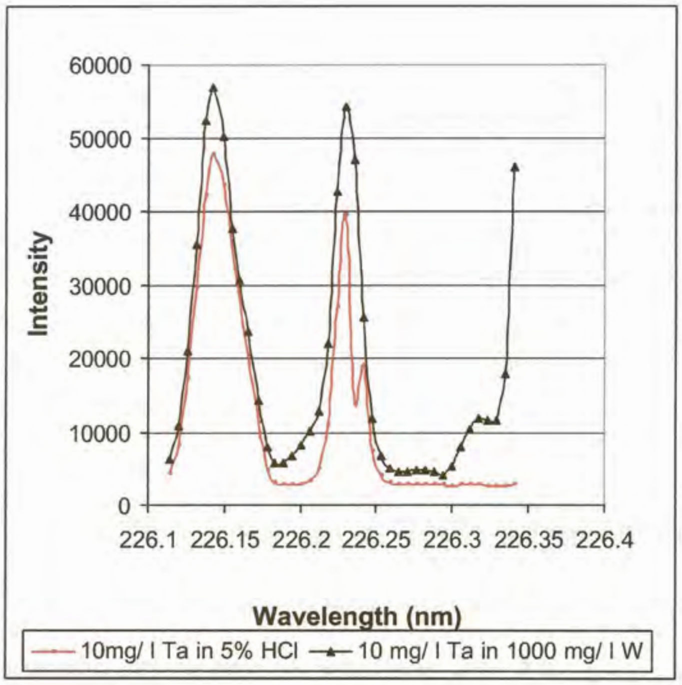

Figure 7.1 : Effect of W on Ta at 226.230 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

At a sample dilution factor of 200, the cobalt concentration in the solution was expected to be in the range 200 to 750 mg/ ℓ, while the tantalum concentration in the same solution was not expected to exceed 10 mg/ ℓ. It can be seen in Figure 7.2 that 500 mg/ ℓ cobalt has very little effect on the measurement of 10 mg/ ℓ tantalum at 226.230 nm but the slight emission from cobalt at 226.260 nm (Harrison, 1969) may cause quantification errors.

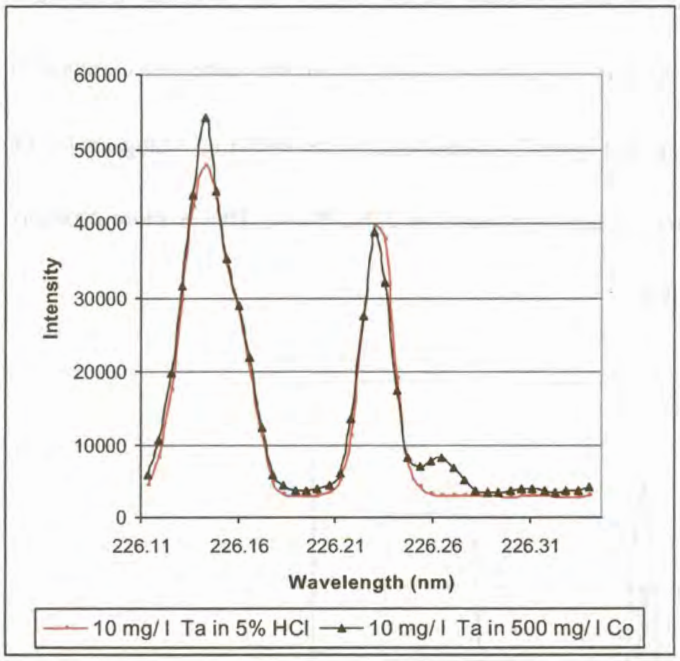

Figure 7.2: Effect of Co on Ta at 226.230 nm (JY-24 ICP-OES, where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

The effect of 500 mg/ ℓ cobalt on the measurement of 10 mg/ ℓ tantalum at 233.198 nm can be seen as a baseline shift in Figure 7.3. This is due to a cobalt emission line at 233.210 nm (Harrison, 1969) and may also cause quantification errors unless the matrices of the calibration solutions are carefully matched to the sample solution matrix.

At the 233.198 nm tantalum emission line, a tungsten emission line occurs at 233.191 nm (Boumans, 1984; Harrison, 1969). The interference can be clearly seen by comparing the emission profiles of 10 mg/ ℓ tantalum in 0.5 M hydrochloric acid and tantalum in 1000 mg/ ℓ tungsten (Figure 7.4). By measuring tantalum at this wavelength in a matrix of tungsten carbide, it would appear as if the tantalum emission peak had shifted to a slightly lower wavelength, while in reality the tungsten emission was being measured. In this way, an erroneous positive result could be obtained for a sample which contained no tantalum.

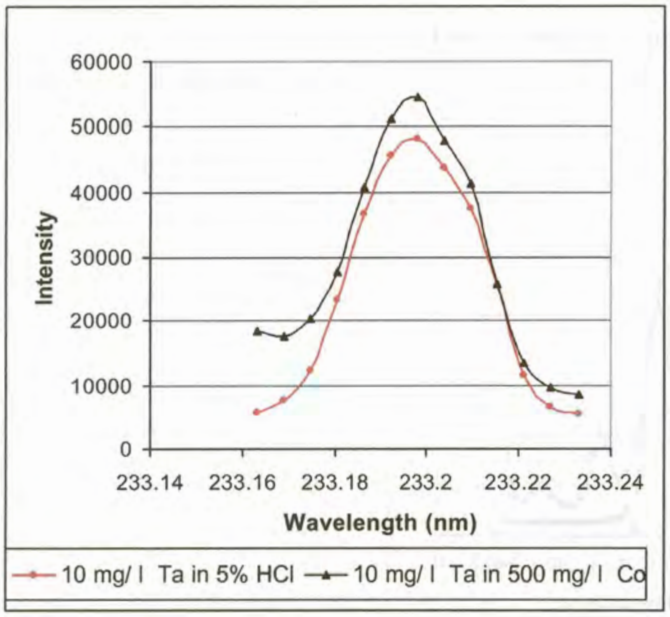

Figure 7.3: Effect of Co on Ta at 233.198 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

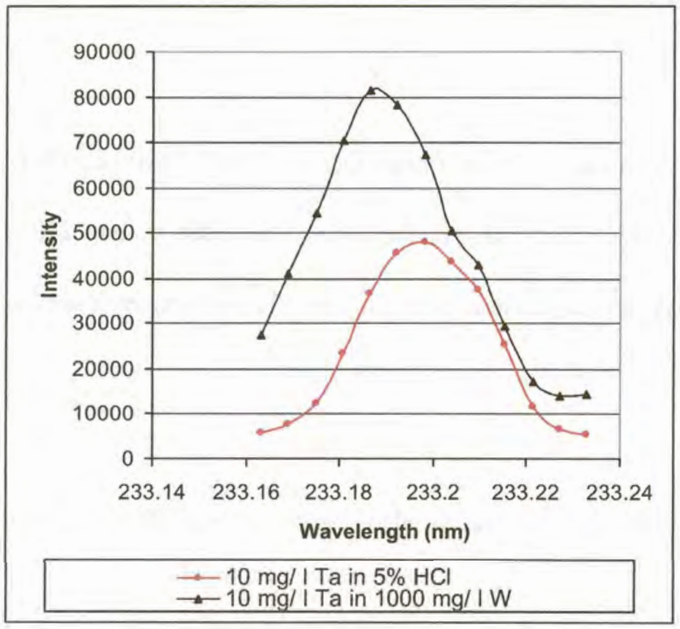

Figure 7.4: Effect of W on Ta at 233.198 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

According to Boumans (1984) and Harrison (1969) there is a fairly strong cobalt emission line at 240.084 nm, near the 240.063 nm tantalum emission line. The effect of 500 mg/ ℓ cobalt on 10 mg/ ℓ tantalum at 240.063 nm is documented in Figure 7.5.

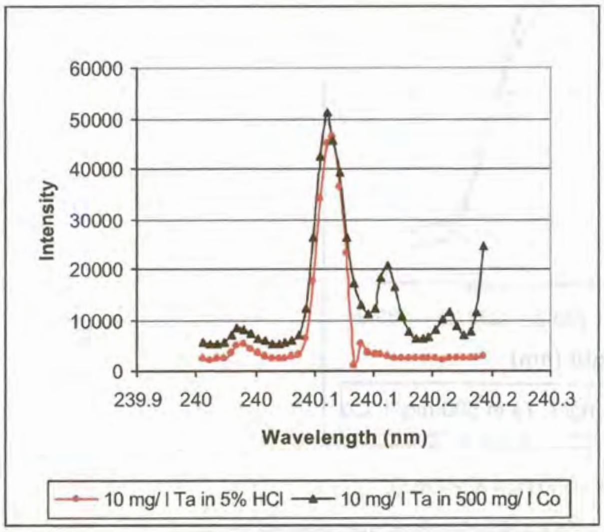

Figure 7.5: Effect of Co on Ta at 240.063 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

There is also a tungsten emission line at 240.130 nm (Boumans, 1984; Harrison, 1969). Emission from this line can clearly be observed in Figure 7.6, as a 'shoulder' at about 240.13 nm. It was found that both cobalt and tungsten interfere slightly with the measurement of tantalum at 240.063 nm.

At 263.654 nm, cobalt at the 500 mg/ ℓ level was found to have only a slight effect on 10 mg/ ℓ tantalum , shown in Figure 7.7.

A weak tungsten emission line at 263.654 nm (Boumans, 1984) has a slight influence on the tantalum emission line at 263.558 nm. The emission profiles of 10 mg/ ℓ tantalum in 0.5 M hydrochloric acid and tantalum in 1000 mg/ ℓ tungsten are compared in Figure 7.8.

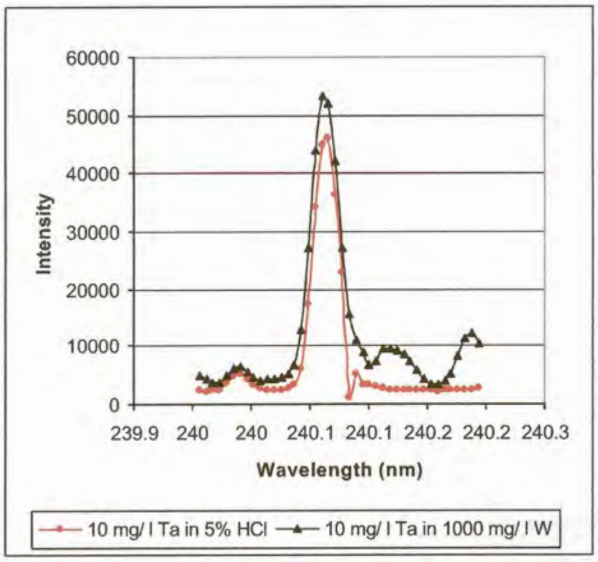

Figure 7.6: Effect of W on Ta at 240.063 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

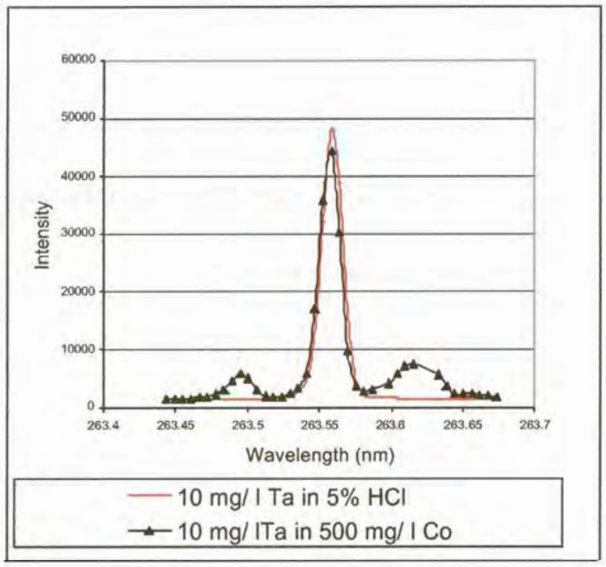

Figure 7.7: Effect of Co on Ta at 263.558 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

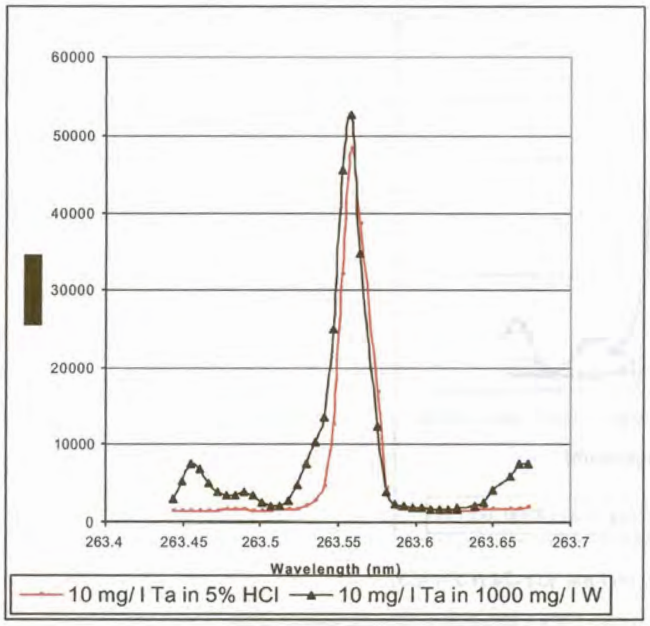

Figure 7.8: Effect of W on Ta at 263.558 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

Cobalt also has an emission line at 268.534 nm (Boumans, 1984; Harrison, 1969), which is near the 268.517 nm tantalum analytical line. A slight interference was confirmed by profiling tantalum solutions in acid against tantalum solutions in 500 mg/ ℓ cobalt (Figure 7.9).

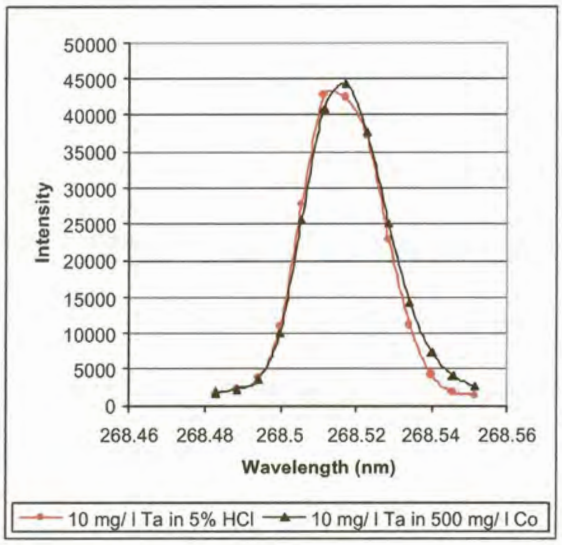

Figure 7.9: Effect of Co on Ta at 268.517 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

However, tungsten at levels of approximately 1000 mg/ ℓ were also found to give rise to emission intensities corresponding to 1 - 3 mg/ ℓ tantalum at 268.517 nm. Boumans (1984) gives no information on emission lines for tungsten in this region but Harrison (1969) documents a tungsten emission line at 268.534 nm The effect can be seen in Figure 7.10.

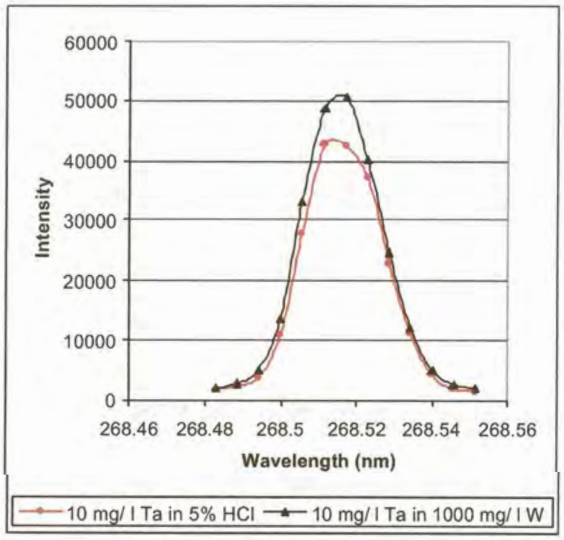

Figure 7.10: Effect of W on Ta at 268.517 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

7.3 CALIBRATION SOLUTIONS

The tantalum concentrations in commercial samples submitted for analysis were found to be below 1 g/ 100 g. This would result in up to 50 mg/ ℓ tantalum in solution, given a dilution factor of 200 when the sample is dissolved as described in Section 4.3. To make matrix matching easier, this solution was diluted by a further factor of 5, giving a sample concentration of 0.5 g/ 500 ml.

As discussed in Section 7.2, the calibration solutions needed to be matrix matched with respect to both cobalt and tungsten. Unfortunately, the tungsten and cobalt stock reference solutions available for analytical use are not compatible. Tungsten is supplied in alkaline solution, while cobalt is supplied in acidic solution. Depending on the pH, either tungsten or cobalt precipitated if the two solutions were mixed. Cobalt forms insoluble cobaltous hydroxide in the alkaline tungsten solution, while tungsten forms insoluble tungstic acid in acid solution. This made proper matrix-matching of the reference solutions very difficult.

It was found, however, that when about 0.6% solid tartaric acid was dissolved in a 1000 mg/ ℓ tungsten solution, which was then acidified with hydrochloric acid, the tungsten remained in solution. The cobalt and tantalum could then be added to the acidified tungsten solution.

The tungsten content in commercial tungsten carbide samples is about 80 g/ 100 g. Normally, a solution of a 0.5 g aliquot of a sample, diluted to 500 ml, was expected to contain about 800 mg/ ℓ tungsten. The approximate tungsten concentration of every sample solution was confirmed by profiling against tungsten at 207.911 nm (a tungsten emission line). Accurate results for tantalum could not be obtained if the tungsten concentration in the analytical solutions exceeded 900 mg/ℓ, since no suitable tungsten solution with a concentration of more than 1000 mg/ℓ was available for matrix-matching.

Three possible solutions to the matrix matching problem were investigated:

i) Tartaric acid was added to a concentrated tungsten solution in ammonia, and the solution acidified with hydrochloric acid. A range of calibration solutions were prepared, each containing 800 mg/ ℓ tungsten, with a cobalt concentration which matched the sample solutions and the appropriate concentration of tantalum for the calibration range. The calibration solutions were also used as quality control samples (QC) between sample solution measurements.

ii) A range of tantalum calibration solutions, matrix matched with cobalt, were prepared. One solution containing tantalum in the same concentration range as the sample solutions, and matrix matched with both cobalt and tungsten was prepared as in method i). The ICP-OES was calibrated with the tantalum solutions containing cobalt, and the solution containing both cobalt and tungsten was used during the run as a quality control (QC) sample. Because tungsten (present in the QC solutions, but not in the calibration solutions) also contributed to the signal at the analytical wavelengths used, the measured concentration of the QC solution was higher than the true concentration. A correction factor was applied to the measured sample concentrations to give the actual concentrations.

iii) The third solution to the problem was to match the tantalum calibration solutions with respect to cobalt and to calibrate the instrument with this range of solutions. The tungsten concentration in sample dilutions of 0.5 g/ 1000 ml was expected to be about 800 mg/ℓ. The emission of a 800 mg/ℓ tungsten solution was measured as a sample at the tantalum wavelengths, and the tungsten measurement value subtracted from the sample measurement values. The calibration solutions could be used as quality control checks for instrument stability between samples during the measurement run but since they did not contain tungsten, no correction was made to the measurements.

Table 7.1 gives a summary of a typical composition of the analytical solution with respect to tantalum, cobalt and tungsten.

Table 7.1:Analytical solution for the analysis of tantalum in tungsten carbide

Analyte	Tantalum
Mass dissolved	0.5 g
Final volume	500 ml
Dilution factor	1000
Concentration tantalum in solution	0 – 8.5 mg/ ℓ
Concentration cobalt in solution	10 – 150 mg/ ℓ
Concentration tungsten in solution	~ 800 mg/ ℓ
Matrix matching of calibration solutions?	Yes, with Co and W (see Section 7.2)

Table 7.2 shows a typical example of a scheme for the preparation of a series of tantalum calibration solutions. In this example, the tantalum solutions are matrix matched with cobalt. A separate quality control solution containing tantalum, cobalt and tungsten at the expected samples concentrations, or a separate solution containing only tungsten could be prepared for quality control use after calibration. A certified 1000 mg/ ℓ tantalum solution, obtained from Merck Chemicals was used. The tungsten and cobalt solutions were also obtained from Merck Chemicals as 1000 mg/ ℓ solutions.

The cobalt concentration in the sample was obtained from the analysis of cobalt, which is normally measured first. If the cobalt concentration in the samples to be measured for tantalum differed by more that 1%, separate quality control standard solutions were prepared. The instrument was calibrated with a series of tantalum solutions, all containing the same concentration of cobalt. Before and after the samples with a different cobalt concentration, a tantalum standard with the appropriate cobalt concentration was analysed and the sample tantalum concentration calculated from these, using a correction factor.

Table 7.2 Preparation of tantalum calibration reference solutions, matrix matched w.r.t. Co: sample tantalum concentration 1 – 5 g/ 100 g and cobalt concentration 9.6 g/ 100 g

Ta concentration required (mg/ ℓ)	Concentration of Ta stock solution (mg/ ℓ)	Volume of Ta stock solution (ml)	*Volume of 1000 mg/ ℓ Co (ml)	Volume of 32% HCl (ml)	Final volume (ml)
0	-	-	5.00	5	100.00
1	20	5.00	5.00	5	100.00
10	1000	1.00	5.00	5	100.00
20	1000	2.00	5.00	5	100.00

* the cobalt concentration in the calibration solutions must be matched to that of the sample solutions, in this case 50 mg/ ℓ

A four point calibration of the JY-24 ICP-OES was performed with the solutions in Table 7.2 at 240.063 nm and 268.517 nm. A typical calibration curve for tantalum at 240.063 nm, with a coefficient of determination (r^2) of 0.9993, was obtained as is shown in Appendix 4, Figure A3. The calibration data was used to calculate the detection limit (LOD) and the quantification limit (LOQ) according to the principles of Miller & Miller (1993). The LOD was calculated to be 1 mg/ ℓ and the LOQ 3 mg/ ℓ.

For the determination of tantalum at 268.517 nm, a calibration curve with a coefficient of determination (r^2) of 0.9999 was obtained, as is shown in Appendix 4, Figure A4. The LOD for this wavelength under the conditions used was found to be 0.4 mg/ ℓ, while the LOQ was 1 mg/ ℓ.

7.4 REFERENCE MATERIALS AND QUALITY CONTROL

A certified cemented carbide reference material, NBS 889, was obtained from NIST (Gaithersburg, USA). The concentration of tantalum in this material was certified as 4.60 ± 0.15 g/ 100 g tantalum.

Two samples of tungsten carbide with only cobalt added (1 to 10 g/ 100 g) and containing no tantalum, were obtained from the Boart Longyear Research Centre (Krugersdorp). These samples were used for spiking experiments.

Since the elemental composition of tungsten carbide tends to vary and the matrix elements may therefore differ from sample to sample, the tantalum measurement may be influenced by these matrix variations. The exact sample composition may not be known beforehand and the matrix effect may not be noticeable when only one analytical wavelength is used. In view of the problems encountered in the analysis of tantalum in tungsten carbide, it was considered advisable to select at least two analytical lines. If the results for the two different lines did not agree to within 5%, an investigation into the effect could have been done and the possibility of reporting an erroneous result avoided.

The method in which the calibration solutions were matched with cobalt only, but where the QC solution contained tantalum, cobalt and tungsten, was shown to be accurate (see Table 7.4). This method was considered less than ideal, especially as the QC solution sometimes blocked the nebulizer, necessitating dismantling of the sample introduction system for cleaning. The whole calibration procedure had to be repeated after reassembling and some time was consequently wasted.

The measurement method that was finally adopted was the one where the matrix of the calibration solutions was matched with cobalt to the same level as that of the sample solutions. A separate solution of tungsten (at the level present in the sample) was measured after calibration of the instrument at 240.063 nm and 268.517 nm. A solution containing 1000 mg/ ℓ tungsten gave a reading of approximately 3 mg/ ℓ at 240.063 nm and approximately 1 mg/ ℓ at 268.517 nm. These values were then subtracted from the sample solution measurements before the final tantalum concentrations in the samples were calculated.

No correction for tungsten was made for the calibration solutions which were used as between-sample QC checks during the measurement run because they did not contain tungsten. The QC solutions were measured to check the instrument stability during the run. Within-run repeatability was considered excellent as a 10 mg/ ℓ tantalum solution gave a reading of 10.31 mg/ ℓ at the beginning of the run at 240.063 nm, and a reading of 10.42 mg/ ℓ at the end of the run, 30 minutes later. At 268.571 nm, the reading was 10.21 mg/ ℓ at the beginning of the run and 10.45 mg/ ℓ at the end of the run.

The effect of the matrix on the measurement of tantalum could be demonstrated by measuring solutions of tungsten carbide which contained no tantalum at different wavelengths. The instrument was calibrated with a series of tantalum solutions in 0.5 M hydrochloric acid and no matrix matching was done. The results of such an experiment are given in Table 7.3.

Table 7.3: Measurement of tantalum without matrix matching at different wavelengths

Sample	**Measured concentration in mg/ ℓ at**	
	226.230 nm	**268.517 nm**
1	36.7	3.5
2	39.4	3.4
3	85.2	3.7

Table 7.3 illustrates the enormous error that can occur if measurements are made without a thorough investigation of matrix effects. None of the samples listed in Table 7.3 did, in fact,

contain tantalum. The difference in the two sets of results also demonstrates that measurement errors and interferences can easily be detected when at least two analytical lines are used for quantitation.

The method in which all the calibration solutions are matched with both cobalt and tungsten was rejected. This method resulted in the use of large volumes of concentrated tungsten solution. Some of these mixtures also caused nebulizer blockages, although no precipitate could be observed. In addition, the preparation of the solutions was more complicated and took longer to prepare than the two other methods.

Tantalum was added to a dissolved tungsten carbide sample which contained no tantalum at a concentration of 4 mg/ ℓ. The ICP-OES was calibrated at 240.063 nm and at 268.517 nm with a series of tantalum solutions, matrix matched with cobalt. The approximate concentration of tungsten in the solution was previously determined by profiling a solution of known tungsten concentration against the sample at 207.911 nm (a tungsten emission wavelength). The tungsten concentration was found to be between 750 and 850 mg/ ℓ in the sample solution (this was consistent with the known composition of the sample). The tungsten solution was then measured at the two tantalum emission wavelengths and the result subtracted from each of the sample measurements before further calculation. An average result for the measurement of tantalum in the spiked sample was 4.2 mg/ ℓ, which is within 5% of the prepared concentration. The tantalum concentration ranges in the sample solutions were found to be between 0 and about 8 mg/ ℓ. The spiking experiment shows that accurate results can be obtained for tantalum at these levels, using the above method.

The highest tantalum concentration measured in tungsten carbide was 0.83 g/ 100 g. This sample was analysed repeatedly, using two of the calibration methods described in Section 7.3. The tantalum concentration in this sample was initially determined to be 0.83 ± 0.06 g/ 100 g, by the analysis of 5 separate aliquots at two wavelengths. The sample was later found to have been analysed by another laboratory; they found the tantalum concentration to be 0.8 g/ 100 g. This sample was then used as a secondary reference material when tantalum was analysed in commercial samples. Table 7.4 shows the two factor ANOVA treatment (Microsoft Excel) of the analytical results obtained for two measurement methods, three sets obtained by the use of a tantalum/ cobalt/ tungsten solution, and three sets obtained by the tungsten emission subtraction method. The analyses were done over an eight month period.

Table 7.4: Two factor ANOVA analysis of tantalum results obtained by two different measurement methods

	Ta (g/ 100 g)	
Method	240.063nm	268.517nm
A	0.776	0.853
A	0.850	0.917
A	0.741	0.895
B	0.802	0.932
B	0.783	0.728
B	0.844	0.728

Method A	Calibration solutions matrix matched with Co. Tungsten measured separately and signal subtracted from results.
Method B	Calibration solutions matrix matched with Co. QC solution matrix matched with Co and W.

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	1.629	0.8145	0.002965
Row 2	2	1.767	0.8835	0.002244
Row 3	2	1.636	0.818	0.011858
Row 4	2	1.734	0.867	0.00845
Row 5	2	1.511	0.7555	0.001512
Row 6	2	1.572	0.786	0.006728
Column 1	6	4.796	0.799333	0.001757
Column 2	6	5.053	0.842167	0.008529

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.0231767	5	0.004635	0.820317	0.58338	5.050339
Columns	0.0055041	1	0.005504	0.974056	0.368992	6.607877
Error	0.0282534	5	0.005651			
Total	0.0569342	11				

No significant difference in the results of the two methods, or the results at the two wavelengths, were observed. The within-wavelength results as well as the between-wavelength results in Table 7.4, show no significant differences. The calculated F values are smaller than F_{crit} in both cases. The average of these results was 0.82 g/ 100 g. The confidence limits were calculated according to the formula (Miller & Miller, 1993):

$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$, where $t_{(0.05,\ 11)} = 2.201$, $s = 0.0719$ and $n = 12$.

The final concentration of 0.82 ± 0.05 g/ 100 g was thus obtained. This is comparable to the initial concentration obtained (0.83 ± 0.06 g/ 100 g) and the value obtained by the external laboratory (0.8 g/ 100 g by XRF).

The certified cemented carbide, NBS 889, was analysed as well, even though its concentration, at 4.60 ± 0.15 g/ 100 g, fell outside the range encountered in commercial samples. Solutions of this material were further diluted to bring the concentration of tantalum in the solution within the calibration range. The matrix of the calibration solutions and quality control solutions had to be adjusted to the lower cobalt and tungsten concentrations in the sample solutions. A measurement result of 4.48 ± 0.32 g/ 100 g was obtained, which is within the uncertainty quoted for the sample.

7.5 DISCUSSION AND CONCLUSIONS

The analysis of the certified reference material, with a relatively high tantalum concentration presented only minor problems. The matrix-matching techniques are capable of minimising the interferences from cobalt and tungsten to a degree where results within 2.5% of the certified value can be obtained. The analysis of the cemented carbide reference sample, NBS 889, also showed that the dissolution procedure, using hydrogen peroxide and aqua regia, is effective in dissolving tantalum in the tungsten carbide.

It was shown that accurate results can be obtained by using the matrix matching technique and there is enough evidence to show that the method produces accurate results even when the samples contain tantalum in concentrations as low as 0.8 g/ 100 g.

It is significant that Piippanen et al (1997a) added tungsten to all the calibration solutions (matrix matching) indicating that they also had problems with tungsten interference. They used the 296.513 nm line for the analysis of tantalum, which was not tested here but it can be assumed that tungsten interferences also occurred at this line.

The sample solutions had to be diluted by a factor of 1000 to bring the tungsten concentration to a level where the matrix of the calibration solutions could be matched (the highest concentration of tungsten solution available was 1000 mg/ ℓ). The quantification limit for tantalum in a solution was found to be between 1 and 3 mg/ ℓ. This meant that tantalum could not be accurately measured in samples which had a tantalum concentration lower than 0.1 g/ 100 g. None of the samples analysed had tantalum concentrations at this level. They either contained no tantalum or tantalum at concentrations above 0.25 g/ 100 g.

In the calibration and correction method finally adopted, there was no wastage of tungsten solution, no nebulizer blockages occurred and the messy, time-consuming complexing/ acidifying step was avoided.

In conclusion it can be said that the dissolution procedure has been proved efficient for the dissolution of tungsten carbide samples when the tantalum concentration is to be analysed. The IC P-OES measurement method, applied as described in this chapter, has also been shown to produce accurate results.