

CHAPTER 8

MEASUREMENT OF TITANIUM

8.1 WAVELENGTHS SELECTED

Thompson & Walsh (1983) recommend the Ti II lines at 337.280 nm and 368.520 nm for titanium analysis. Both these lines were investigated and subsequently used for analysis of titanium in a matrix of tungsten carbide.

Pippannen et al (1997a) used the Ti II line 332.676 nm for titanium analysis. Harrison (1969) reported tungsten emission lines at 332.642 nm and 332.762 nm., and strong cobalt emission lines at 332.656 nm and 332.700 nm.

8.2 MATRIX EFFECTS AND INTERFERENCES

On profiling a 10 mg/ℓ titanium solution in 0.5 M hydrochloric acid against a solution of 10 mg/ℓ titanium in 500 mg/ℓ cobalt a serious interference was observed using the 332.676 nm titanium emission line, as can be seen in Figure 8.1. The likely cause was thought to be the cobalt emission line at 332.700 nm, reported by Harrison (1969).

In addition, the effect of the tungsten emission lines at 332.642 nm and 332.762 nm on titanium measurements, also reported by Harrison (1969), can be clearly observed in Figure 8.2. Measurements for titanium made at 332.676 nm without careful matrix matching may result in erroneously positive titanium results or incorrect quantitation results.

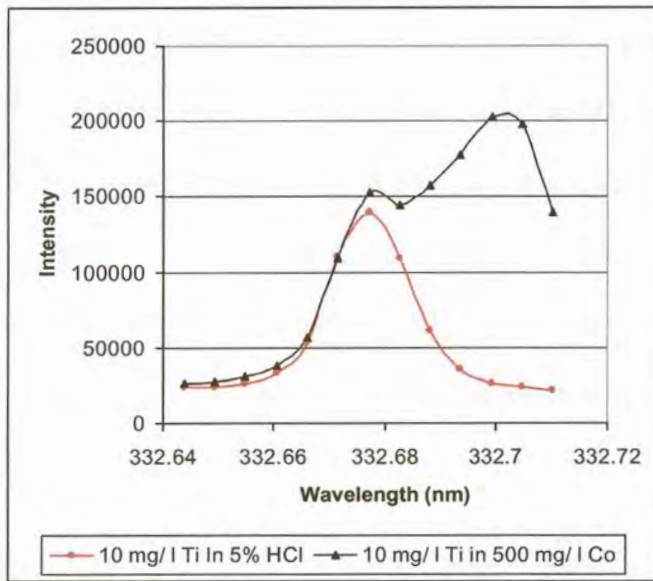


Figure 8.1: Effect of Co on Ti at 332.676 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

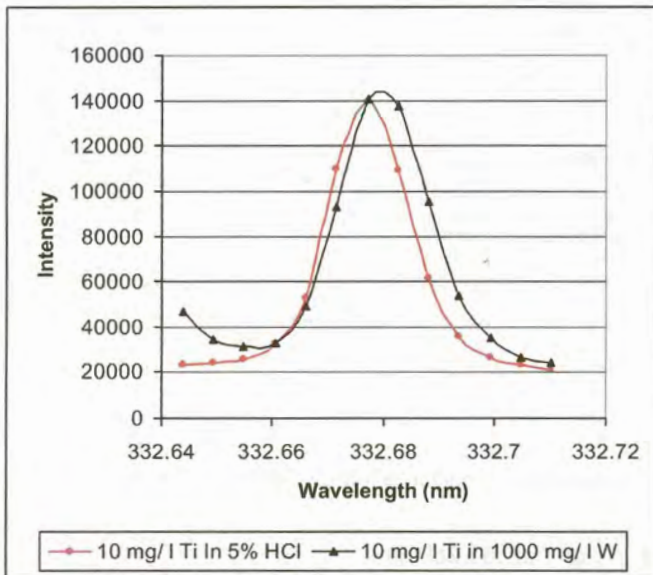


Figure 8.2: Effect of W on Ti at 332.676 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

No interferences from cobalt or tungsten are reported for the 337.280 nm titanium emission line (Boumans, 1984; Harrison, 1969). On profiling solutions of titanium in various matrices, it was experimentally confirmed that tungsten, titanium, tantalum, chromium and vanadium have negligible influence on titanium measurements. However, cobalt was found to slightly affect the measurement of titanium at 337.280 nm (Figure 8.3) and to obtain quantitative results matrix matching of the calibration solutions with respect to cobalt was performed.

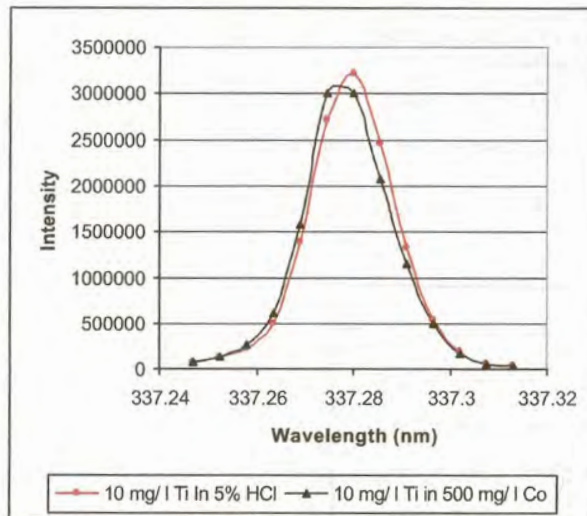


Figure 8.3: Effect of Co on Ti at 337.280 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

As can be seen from Figure 8.4, tungsten at a concentration of 1000 mg/ℓ has only a slight effect on a solution of titanium of 10 mg/ℓ at 337.280 nm.

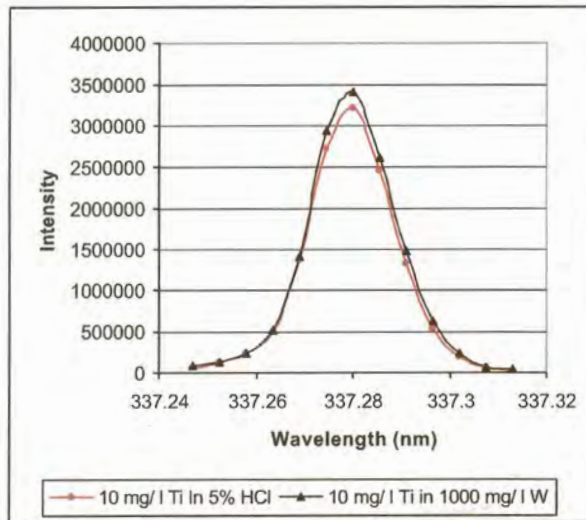


Figure 8.4: Effect of *W* on Ti at 337.280 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

Although Boumans (1984) gives no information of a cobalt emission line near 368.520 nm and Harrison (1969) mentions only a cobalt emission line at 368.496 nm, cobalt at the 500mg/ℓ level was found to have an effect on the titanium measurement at this wavelength, as is illustrated in Figure 8.5.

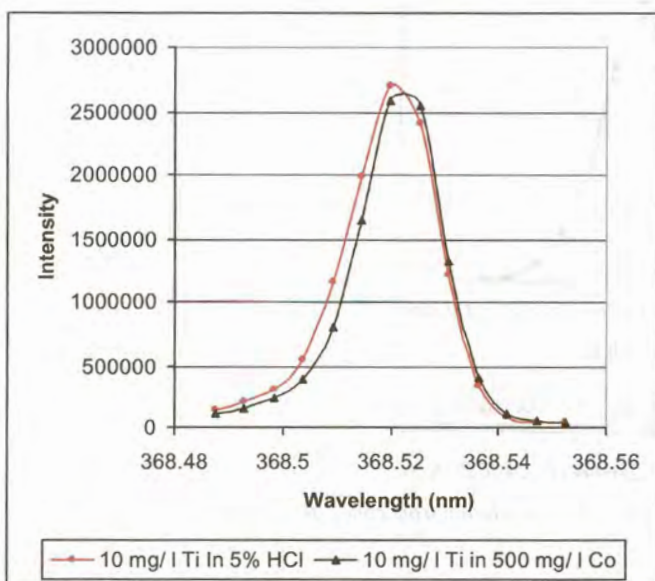


Figure 8.5: Effect of Co on Ti at 368.520 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

A tungsten emission line is reported by Harrison (1969) at 368.502 nm and this was observed to have a slight effect on the titanium measurement at 368.520 nm (Figure 8.6).

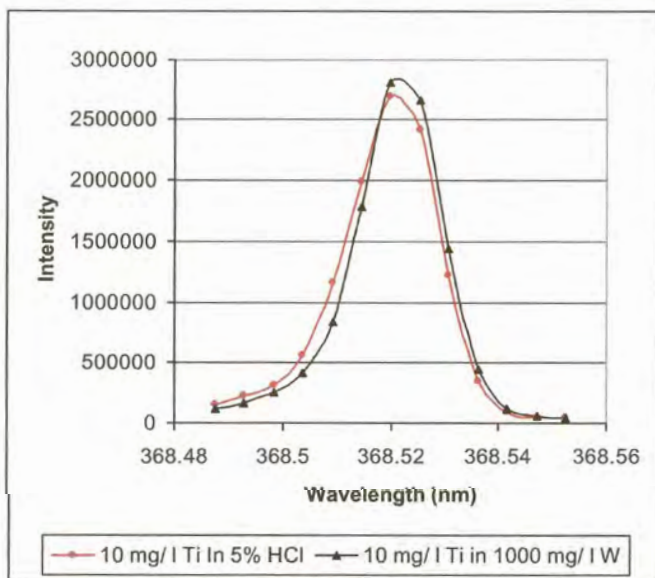


Figure 8.6: Effect of W on Ti at 368.520 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

8.3 CALIBRATION SOLUTIONS

The titanium content of the commercial samples analysed during this study was found to be below 0.02 mg/ 100 g. To test the efficiency of the dissolution method for titanium, a certified reference material of cemented carbide, NBS 889 obtained from NIST (USA) was analysed. The certified titanium concentration was 4.03 ± 0.10 g/ 100 g. The measurement method for tungsten carbide samples containing titanium in the range 0 to 1 g/ 100 g was tested by titanium spiking of solutions of tungsten carbide which contained no titanium.

Initially, calibration solutions were prepared which matched the matrix of a solution of the NBS 889 cemented carbide with respect to cobalt. The sample dilution factor was 2000, with the solution cobalt concentration roughly 50 mg/ ℓ.

Table 8.1 gives a summary of a typical composition of the analytical solution with respect to titanium, cobalt and tungsten.

Table 8.1: Solution for the analysis of titanium in tungsten carbide

Analyte	Titanium
Mass dissolved	0.5 g
Final volume	1000 ml
Dilution factor	2000
Concentration titanium in solution	~ 20 mg/ ℓ
Concentration cobalt in solution	5 – 75 mg/ ℓ
Concentration tungsten in solution	~ 450 mg/ ℓ
Matrix matching of calibration solutions?	Yes (see above)

Table 8.2 gives a summary of a typical scheme for the preparation of a typical range of

calibration solutions for titanium analysis. The titanium and cobalt solutions were obtained as a certified 1000 mg/ℓ solutions from Merck Chemicals.

Table 8.2: Preparation of titanium calibration reference solutions: sample titanium concentration 2-4 g/100 g and cobalt concentration 9.6 g/100 g.

Ti concentration required (mg/ℓ)	Concentration of Ti stock solution (mg/ℓ)	Volume of Ti stock solution (ml)	Volume of 1000 mg/ℓ *Co (ml)	Volume 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
50	1000	5.00	5.00	5	100.00

* The cobalt concentration must match those of the sample solutions

A four point calibration of the ICP-OES was performed with the solutions in Table 8.2 at 337.280 nm and 368.520 nm.

At 337.280 nm, a calibration curve with a coefficient of determination (r^2) of 0.9999, was obtained. This curve can be viewed in Appendix 4, Figure A5. The limit of detection (LOD), calculated from this data according to the principles of Miller & Miller (1993), was 0.3 mg/ℓ and the limit of quantification (LOQ) 1 mg/ℓ.

The calibration curve at 368.520 nm, with a coefficient of determination (r^2) of 0.9999, can be viewed in Appendix 4, Figure A6. The LOD, calculated from this data, was 0.2 mg/ℓ and the limit of quantification 0.7 mg/ℓ.

When other titanium calibration series, with the highest titanium concentrations respectively 10

and 20 mg/ ℓ, were used for calibration, the r^2 value was never below 0.9999 and the LOQ never above 1 mg/ ℓ.

8.4 REFERENCE MATERIALS AND QUALITY CONTROL

The effect of cobalt and tungsten in the matrix on the measurement of titanium was checked by preparing solutions of titanium (10 mg/ ℓ) in respectively 0.5 M hydrochloric acid, 9000 mg/ ℓ tungsten, 50 mg/ ℓ cobalt, and a 10 mg/ ℓ mixture of chromium, tantalum and vanadium. These solutions were measured at 337.280 nm and 368.520 nm after calibration of the ICP-OES with titanium solutions in 5 % hydrochloric acid. The results are tabulated in Table 8.3.

Table 8.3: Measured effect of W, Co, Cr, Ta and V on titanium measurements

Matrix of the 10 mg/ ℓ titanium solution	Measured concentration of Ti (mg/ ℓ) at	
	337.280 nm	368.520 nm
0.5 M HCl	10.0	10.0
1000 mg/ ℓ W	9.9	10.3
50 mg/ ℓ Co	10.8	10.7
10 mg/ ℓ Cr, Ta, V	9.5	9.6

The data in Table 8.3 confirms the observations made regarding the effect of cobalt in Section 8.2. At both wavelengths, the measured titanium concentration was higher than expected when measured in a cobalt matrix. In both cases, the difference is more than 5% of the prepared concentration and the calibration solutions for the measurement of titanium were matrix matched with respect to cobalt. A slight interference by tungsten on titanium measurements was observed at 337.280 nm and 368.520 nm in Section 8.2. From the data in Table 8.3, it can be seen that the effect is negligible, since the measurements for titanium made in a tungsten matrix, were within 5% of the prepared concentration. The calibration solutions were therefore not matrix

matched with respect to tungsten.

The concentration of titanium in the cemented carbide reference material, NBS 889, is certified as $4.03 \text{ g} \pm 0.10 \text{ g/100 g}$. On measurement of the titanium in triplicate aliquots of this reference material, dissolved by the hydrogen peroxide/ aqua regia method described in Section 4.3, a titanium concentration of $3.96 \pm 0.17 \text{ g/100 g}$ was obtained. The dilution factor for the analysis was 2000, when 0.5 g sample was diluted to 1000 ml, giving a titanium concentration in the solutions of about $20 \text{ mg/}\ell$. The titanium concentrations obtained are tabulated in Table 8.4.

Table 8.4: Ti measurement results for cemented carbide NBS 889

	Concentration Ti (g/ 100 g) measured at		Average
	337.280 nm	368.520 nm	
Aliquot 1	3.85	3.95	3.90
Aliquot 2	3.96	3.94	3.95
Aliquot 3	4.03	4.03	4.03
Average			3.96
s (n = 6)			0.0669

The confidence limits for the results in Table 8.4 were calculated according to the formula (Miller & Miller, 1993):

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}, \text{ where } \bar{x} = 3.96, t_{(0.05, 5)} = 2.5706, s = 0.0669 \text{ and } n = 6$$

giving a titanium concentration of $3.96 \pm 0.17 \text{ g/100 g}$. Since the certified concentration was given as $4.03 \pm 0.10 \text{ g/100 g}$, the results prove that the method is effective for the dissolution of titanium in tungsten carbide.

When solutions of tungsten carbide, prepared from titanium-free material, were spiked with $0.2 \text{ mg/}\ell$ titanium, measured concentrations (after calibration with cobalt matched titanium solutions)

of 0.166 and 0.171 mg/ℓ were obtained, at 337.280 nm and 368.520 nm respectively. The dilution factor for the solutions was 200, giving a cobalt concentration of about 250 mg/ℓ in the solutions. Since the solutions were measured below the theoretical detection limit (Section 8.3), the results could be considered excellent. Other aliquots of the same solutions were spiked with 5 mg/ℓ titanium and measurement results of 4.475 and 4.537 mg/ℓ at the two wavelengths, respectively, were obtained. These concentrations are within 5% of the prepared concentration and accurate quantitation of titanium levels in samples with titanium concentrations between 0.01 and 1 g/100 g can realistically be expected to be achieved.

The measurement runs for titanium were always shorter than 30 minutes. A reference solution of titanium (QC) was always analysed at the beginning of an analytical run and at the end. The results for these measurements were always found to be within 5% of each other.

8.5 DISCUSSION AND CONCLUSIONS

Although none of the commercial samples contained titanium in measurable concentrations, there was enough data to calculate that titanium concentrations as low as 0.01 g/ 100 g in the sample could be analysed without major problems. No false positive results were obtained using the measurement methods described in this chapter.

The certified titanium concentration of the NBS 889 material was 4.03 ± 0.10 g/ 100 g. An analytical concentration of 3.96 ± 0.17 g/ 100 g was obtained, using the above method. This falls within the certified uncertainty range. The results also show that titanium in tungsten carbide is effectively dissolved by the hydrogen peroxide/ aqua regia method.

As shown during the analysis of cobalt and tantalum, it is good analytical practice to use at least two different analytical wavelengths for ICP-OES analyses if time permits. If samples of exactly the same elemental composition are routinely analysed, either wavelength may be used after validation. Although no evidence was found during the measurement of titanium that other elements influence the measurements, the range of different experimental tungsten carbide samples received by the laboratory justified the use of both analytical wavelengths for all the analyses.