CHAPTER 6

MEASUREMENT OF COBALT

6.1 WAVELENGTHS SELECTED

According to the Thompson and Walsh (1983), the most common line used for cobalt analysis is the Co II line at 228.616 nm. This is the line used by Piippanen et al (1997a) for the measurement of cobalt in a tungsten carbide matrix. Thompson and Walsh also cited the cobalt line at 238.346 nm as relatively sensitive and interference-free. However, vanadium emits weakly at 238.892 nm and tantalum has a strong line at 238.346 nm (Boumans, 1984).

The lines 228.616 nm and 238.346 nm were evaluated for suitability for the measurement of cobalt in a tungsten carbide matrix.

6.2 INVESTIGATION OF MATRIX EFFECTS AND INTERFERENCES

Before quantitative measurements could be made, it was necessary to determine the effect of the matrix elements present in the solution on the measurement of cobalt at the chosen analytical wavelengths. These elements were tungsten, tantalum, titanium, vanadium and chromium. In order to study these effects, 10 mg/ ℓ cobalt was prepared by serial dilution of the 1000 mg/ ℓ Merck stock solution in each of the following matrices:

i)   0.5 M hydrochloric acid (a 5% dilution from concentrated 32% hydrochloric acid)

ii)   1000 mg/ ℓ tungsten

iii) 10 mg/ ℓ of tantalum, titanium, vanadium and chromium in 0.5 M hydrochloric acid

iv) 10 mg/ ℓ of tantalum, titanium, vanadium and chromium in 1000 mg/ ℓ tungsten.

Because the tungsten concentration in a commercial tungsten carbide sample was expected to be approximately 1000 mg/ ℓ in the prepared solution when the cobalt concentration in the solution was about 10 mg/ ℓ, the effects at these concentrations were studied. The emission intensities of 10 mg/ ℓ cobalt in the two different matrices (0.5 M hydrochloric acid and 1000 mg/ ℓ tungsten) were measured at 228.616 nm and 238.346 nm and compared. It was found that the tungsten matrix of the solution did not have a large influence on the emission intensity of cobalt at either of the two analytical lines. It was therefore not deemed necessary to matrix match the cobalt calibration solutions with tungsten. Accurate results were obtained when a certified reference material of cemented tungsten carbide was analysed without matrix-matching (see Table 6.3). The profiles are shown in Figure 6.1 and Figure 6.2. In these profiles and those in the sections which follow, relative emission measurements are shown, that is, they are dependant on the adjustments made to optimise the element signal at that wavelength. The comparisons in a given figure were made with the same adjustment settings.
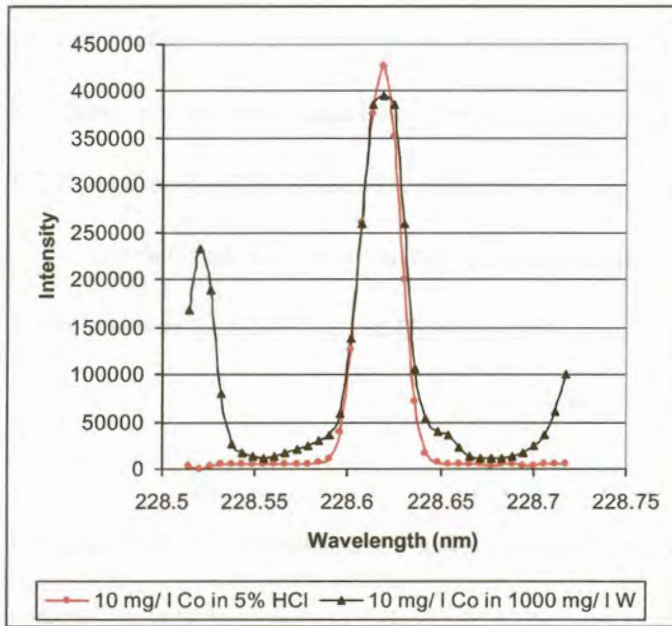
Figure 6.1: The effect of W on Co at 228.616 nm (JY-24 ICP-OES),

where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)
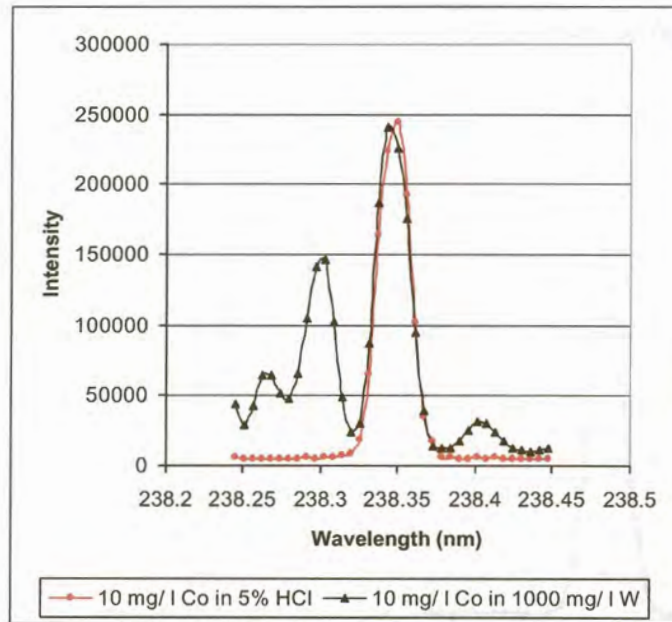

Figure 6.2: The effect of W on Co at 238.346 nm (JY-24 ICP-OES),

where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

When 10 mg/ ℓ cobalt was mixed with respectively 10 mg/ ℓ of chromium, vanadium, tantalum and titanium, the comparison of their emission profiles showed that tantalum and titanium at these levels have no significant effect on the emission intensity of cobalt at 228.616 nm and 238.346 nm. However, chromium and vanadium showed a tendency to enhance the cobalt signal. This may be because of a chromium emission line at 238.333 nm, and vanadium emission lines at 228.659 nm 238.344 nm (Harrison, 1969).

The emission profiles and intensities of 10 mg/ ℓ cobalt in 0.5 M hydrochloric were compared at 228.616 nm and 238.346 nm to those of 10 mg/ ℓ cobalt in a matrix of 10 mg/ℓ tantalum, titanium, vanadium and chromium in 0.5 M hydrochloric acid. Figure 6.3 and Figure 6.4 show that the emission is apparently slightly enhanced at both wavelengths when tantalum, titanium, vanadium and chromium are added to the cobalt solution.
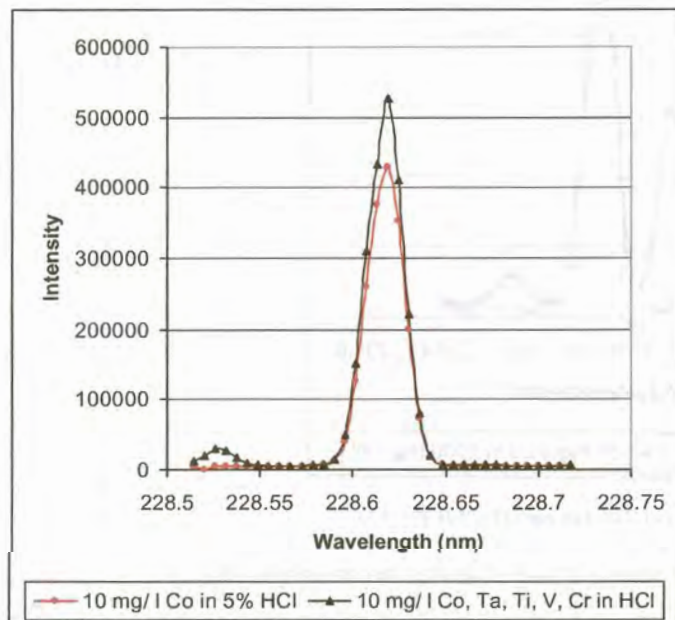

Figure 6.3 : Effect of Ta, Ti, V, Cr on Co at 228.616 nm (JY-24 ICP-OES),
where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)
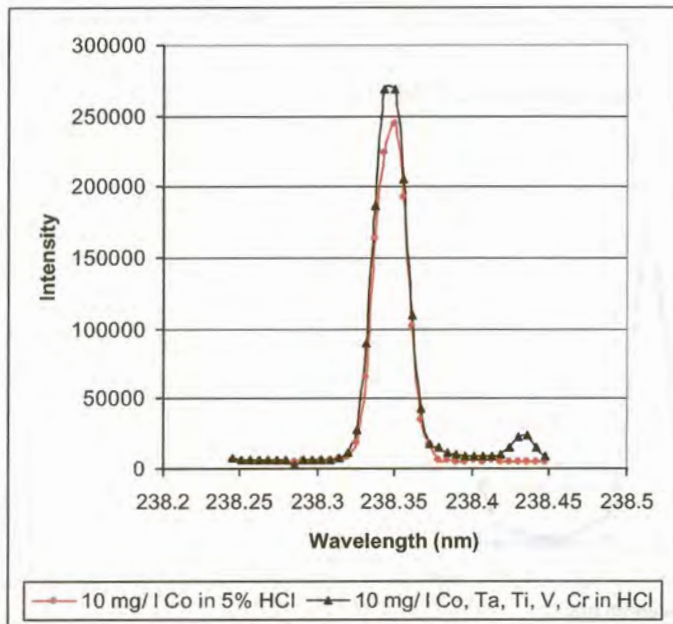
Figure 6.4: Effect of Ta, Ti, V, Cr on Co at 238.346 nm (JY-24 ICP-OES),
where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

Since chromium and vanadium were previously found to influence the emission, it was necessary to matrix-match the calibration solutions with vanadium and chromium when these elements were also present in sample solutions at 10 mg/ ℓ levels. In practise, none of the tungsten carbide samples analysed contained chromium or vanadium in concentrations above 1 g/ 100 g in the powder. This would typically result in a maximum solution concentration of 1 mg/ ℓ of chromium or vanadium when the cobalt concentration in solution is 10 mg/ ℓ. With solutions of the above composition, it was found that the effect of chromium and vanadium on the measurement of cobalt was negligible and matrix-matching of the calibration solutions was not required.

The matrix of the above solution (10 mg/ ℓ cobalt, tantalum, titanium, vanadium and chromium) was modified to 1000 mg/ ℓ tungsten instead of 0.5 M hydrochloric acid. To test the effect on

tungsten on the emission at both analytical wavelengths, the profiles of the two solutions were compared. From Figure 6.5, it can be seen that tungsten at the 1000 mg/ ℓ level had no significant effect on the measurement of cobalt at 228.616 nm.
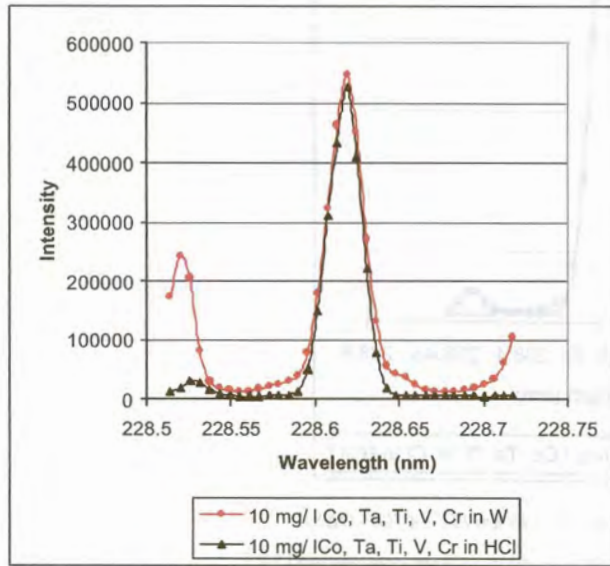

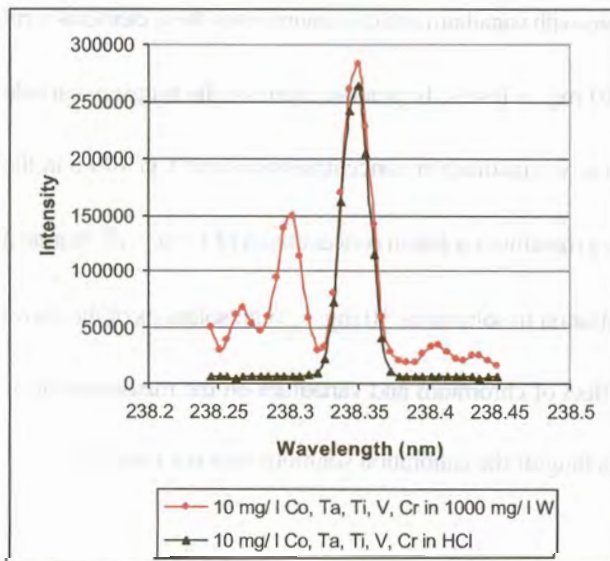*Figure 6.5: Effect of W on Co, Ta, Ti, Cr at the Co emission wavelength 228.616 nm (JY-24 ICP-OES)*

Figure 6.6: Effect of W on Co, Ta, Ti, Cr at the Co emission wavelength 238.346 nm (JY-24 ICP-OES)

There are tungsten emission lines at 238.320 nm and 238.354 nm (Harrison, 1969) and these can be observed in the profiles in Figure 6.6. It will be demonstrated in Section 6.4 that accurate measurements of cobalt were still obtained without matrix matching.

The above result (Figure 6.6) shows that even with tantalum, titanium, vanadium and chromium present in the solution at the maximum expected levels, tungsten has no effect on the measurement of cobalt. This experiment also confirms the results obtained when mixtures containing only cobalt and tungsten were measured. It was therefore not necessary to add tungsten to the calibration solutions during the measurement of cobalt in tungsten carbide solutions. Evidence of a baseline shift may be seen in Figure 6.6, which may result in false positive results for cobalt. However, the analysis is performed at two analytical lines and there would be a significant difference in the concentrations between the two wavelengths if no cobalt was, in fact, present in the sample. According to the quality control procedures the results would not be reported until the cause of the discrepancy had been investigated.

6.3 CALIBRATION SOLUTIONS

In the sample dissolution step, described in Section 4.3, the powdered tungsten carbide was initially diluted by a factor of 200 (0.5 g/ 100 ml). The concentration of cobalt in these solutions was consequently in the range 200 mg/ ℓ to 750 mg/ ℓ. This is much higher than the concentrations of the other elements of interest and therefore the solution was diluted further, and cobalt was analysed separately from the other elements.

According to Jobin Yvon Emission Instruments S.A., the JY-24 ICP-OES has a linear measurement range from 0 to 1000 mg/ ℓ for most elements. However, Miller & Miller (1993:

113) have shown that the most accurate results (i.e. those with the least error associated with them) are made in the middle portion (centroid) of the calibration curve. If all the elements were to be measured in the same solution, cobalt would be present at very high concentrations (say, 750 mg/ ℓ) while elements like vanadium, for example, would be present at relatively low concentrations (about 1 mg/ ℓ). This would clearly result in almost no measurements in the middle of the calibration curve, which would not be analytically desirable. The sample solutions for cobalt analysis were therefore further diluted by a factor of 10 with 0.5 M hydrochloric acid, bringing the cobalt concentration into the 20 to 75 mg/ ℓ range.

A summary of the composition of the analytical solution with respect to cobalt and tungsten is given in Table 6.1.

Table 6.1: Analytical solution for the analysis of cobalt in tungsten carbide

Analyte	Cobalt
Sample mass dissolved	0.5 g
Final sample volume	1000 ml
Dilution factor	2000
Concentration cobalt in sample solution	25 – 75 mg/ ℓ
Concentration tungsten in sample solution	~ 450 mg/ ℓ
Matrix matching for calibration solutions?	None required

A series of four calibration solutions were prepared from a 1000 mg/ ℓ Merck certified cobalt reference solution. The exact concentrations are indicated in Table 6.2 and cover the whole range of possible cobalt concentrations in the sample solutions.

Table 6.2: Preparation of Co calibration reference solutions

Cobalt concentration required (mg/ ℓ)	Concentration of Co stock solution (mg/ ℓ)	Volume of Co stock solution (ml)	Volume of 32% HCl (ml)	Final volume (ml)
0	-	-	5	100.00
10	100	10.00	5	100.00
50	1000	5.00	5	100.00
100	1000	10.00	5	100.00

The JY-24 ICP-OES was calibrated with the calibration solutions in Table 6.2 at 228.616nm and 238.346 nm. A typical calibration curve, with a squared product-moment correlation coefficient (r^2) of 0.9998, was obtained for the 228.616 nm line. A plot of the data, given in Appendix 4, Figure A1, shows a linear curve. The limit of detection was calculated from this data, using the statistical principles of Miller and Miller (1993). A limit of detection (LOD) for the 228.616 nm line was found to be 2 mg/ ℓ while the quantification limit was found to be 7 mg/ ℓ. Since the measured cobalt concentrations in the analytical solutions were in the range 25 to 75 mg/ ℓ , the calibration range was considered to be correct.

For the 238.346 nm line, a typical calibration curve with a squared product-moment correlation coefficient (r^2) of 0.9999 was obtained. The curve, which was demonstrably linear, is shown in Appendix 4, Figure A2. The limit of detection (LOD) for the 238.346 nm line was found to be 1 mg/ ℓ, while the quantification limit was found to be 4 mg/ ℓ.

6.4   REFERENCE MATERIALS AND QUALITY CONTROL

A standard reference material of powdered cemented carbide (NBS 889) with a certified cobalt concentration of 9.50 ± 0.15 g/ 100 g, was obtained from NIST, USA. The certificate of

analysis for this material is included under Appendix 3. It was analysed with several commercial samples over a period of two years. The results are summarized in Table 6.3.

Table 6.3: Analytical results for cobalt in cemented carbide NBS 889

Co concentration (g/100 g)	Number of aliquots analysed
9.48 ± 0.58	2
9.29 ± 0.25	2
9.17 ± 0.50	1
9.56 ± 0.34	2
9.86 ± 0.19	2
9.62 ± 0.25	2
9.66 ± 0.17	1
9.30 ± 0.48	3
Mean 9.51	
Std dev (s) 0.2858	
RSD (%) 3.01	
Confidence limits ± 0.58	

Where the number after the ± symbol was calculated according to the formula

$\mu = \bar{x} \pm \dfrac{ts}{\sqrt{n}}$ (Miller & Miller, 1993). For each aliquot analysed, the solution

was measured at two different wavelengths; n in the formula is thus equal to 2 times the number of aliquots analysed.

The final mean, standard deviation, RSD and confidence limits in Table 6.3 were calculated according to the principles of Miller and Miller (1993) from 30 cobalt measurement values. The confidence limits were also calculated according to the formula

$$\mu = \bar{x} \pm \dfrac{ts}{\sqrt{n}}$$

where s = 0.286, n = 30 and $t_{(0.05, 29)}$ = 2.045.

All the values in Table 6.3, except 9.86 ± 0.19 g/ 100 g, fall within the certified range of the NBS 889 reference material. The average cobalt concentration of the 15 analyses, at 9.51 ± 0.58 g/ 100 g, also falls in the certified range. The confidence limits for the ICP-OES

measurements are much larger than those of the certified range ($\pm$ 0.58 vs $\pm$ 0.15 g/ 100 g). In a commercial laboratory, it is often difficult to include sufficient replicate analyses of a sample for complete statistical analysis of the results. This is due to financial and time constraints and was also the case with these analyses. Dixon's Q ratio, to determine if the value 9.86 is an outlier, was found according to the formula:

Q = |suspect value – nearest value| / (largest value – smallest value)

which gives Q = (9.86 – 9.66)/ (9.86 – 9.17) = 0.29

From tables (Miller & Miller, 1993) the critical value of Q is given as 0.524 for n = 8 (P=0.05). The calculated value does not exceed this, so statistically 9.86 is not an outlier.

To test if there is a significant difference in the measurement results obtained at the two different wavelengths, a single factor ANOVA analysis was performed, using a Microsoft Excel spreadsheet. This spreadsheet is shown in Table 6.4. The calculated F value for the between group variation is 1.481, while the critical F value for a 95% level of confidence is 4.600. Since F_{crit} is larger than $F_{1,14}$ this is an indication that there is no significant difference between the results obtained for the different wavelengths.

Table 6.4: Single factor ANOVA analysis on cobalt results for two wavelengths

Analysis no.	Cobalt (g/100 g)	
	228.616nm	238.346nm
1	9.715	9.235
2	9.384	9.197
3	9.286	9.053
4	9.614	9.507
5	9.569	9.662
6	9.841	9.879
7	9.701	9.622
8	9.409	9.158

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Column 1	8	76.519	9.564875	0.036361
Column 2	8	75.313	9.414125	0.086376

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.09090225	1	0.090902	1.481258	0.243697	4.600111
Within Groups	0.85915575	14	0.061368			
Total	0.950058	15				

To check the instrument stability, a quality control (QC) solution of a known concentration of cobalt was analysed after every third sample solution during a run. If only one or two samples were analysed during the run, a QC solution was measured after every second sample. On Jobin Yvon and Varian measurement validation software for ICP-OES, a quality control limit of ±5% for measurement of a sample of known concentration is usually set. Measurements within 5% of the prepared value are deemed acceptable. Therefore, if the measured concentration, after instrument calibration, differed more than 5% from the prepared concentration (Table 6.2), the instrument was recalibrated with the calibration solutions and the run repeated. In Table 6.5, a typical spread of between-sample measurement results for a 10 mg/ ℓ cobalt QC solution is analysed by a two-factor ANOVA, using a Microsoft Excel spreadsheet.

Table 6.5: ANOVA analysis of typical results for a between-sample QC solution of 10 mg/ ℓ cobalt over a period of approximately 90 minutes.

	Measured Co concentration (mg/l)	
	228.62nm	238.35nm
1	9.651	9.927
2	9.874	10.04
3	9.806	9.95
4	9.793	9.591
5	9.612	9.651
6	10.15	9.999
7	9.873	10.145
8	9.78	9.668
9	9.753	9.608
10	10.27	9.943
11	10.14	9.892

Anova: Two-Factor Without Replication

SUMMARY	Count	Sum	Average	Variance
Row 1	2	19.578	9.789	0.038088
Row 2	2	19.914	9.957	0.013778
Row 3	2	19.756	9.878	0.010368
Row 4	2	19.384	9.692	0.020402
Row 5	2	19.263	9.6315	0.000761
Row 6	2	20.149	10.0745	0.011401
Row 7	2	20.018	10.009	0.036992
Row 8	2	19.448	9.724	0.006272
Row 9	2	19.361	9.6805	0.010513
Row 10	2	20.213	10.1065	0.053464
Row 11	2	20.032	10.016	0.030752
Column 1	11	108.702	9.882	0.045608
Column 2	11	108.414	9.855818	0.036967

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	0.596726	10	0.059673	2.605564	0.073431	2.97824
Columns	0.00377	1	0.00377	0.164623	0.693481	4.964591
Error	0.22902	10	0.022902			
Total	0.829516	21				

In the case of between-wavelength variations (columns, Table 6.5) as well as between-measurement variations (rows, Table 6.5), the calculated F value is smaller than F_{crit} for a 95% level of confidence, indicating that there were no significant differences in the measurement results. A run time for a typical ICP-OES analysis of cobalt in tungsten carbide is usually more than an hour when 5 to 10 samples are analysed in duplicate and the sample matrix, because of its complexity, may cause changes in the sample introduction system of the instrument (nebulizer clogging, memory effects, torch deposits). The results in Table 5.5 show that the instrument was stable during the entire measurement run. This is an indication that the sample measurement solutions (commercial tungsten carbide solutions, produced by the hydrogen peroxide dissolution method) are not contributing to clogging by precipitation of tungsten complexes.

All the samples were dissolved at least in duplicate. If the final cobalt concentrations of the two aliquots were not within 5% of each other, additional aliquots were dissolved and analysed.

Some of the sample solutions were also reanalysed at the end of the measurement run to check the within-run repeatability. The initial measurements for two samples during different measurements runs are listed in Table 6.6, together with measurements of the same samples approximately one hour later without re-calibration of the instrument. The results for the initial and subsequent measurements of each sample are within 5% of each other. Similar results to those in Table 6.6 were obtained for all the samples analysed for cobalt by this method.

Table 6.6: Within-run repeatability of sample measurements for cobalt in tungsten carbide

Measurement of:	Measured Co concentration from raw data (mg/ ℓ)	
	at 228.616 nm	at 238.346 nm
Sample 1, initial	23.81	23.12
Sample 1, 60 min later	24.27	23.76
Sample 2, initial	30.48	30.23
Sample 2, 60 min later	31.36	30.51

The elemental composition of tungsten carbide tends to vary. Some batches may contain iron, other experimental elements or the concentrations of the known elements may vary. The cobalt measurement may therefore be influenced by these matrix variations. Since the effect may not be noticeable when only one analytical wavelength is used, it was found prudent to select at least two analytical lines per element. If the results were found to differ by more than 5% using the two specified lines, an unforeseen interference may have been the cause and an investigation could have been done. No such effect was, in fact, observed.

6.5   DISCUSSION AND CONCLUSIONS

All except two of the results (9.17 g/ 100 g and 9.86 g/ 100 g) in Table 6.3 for the analysis of cobalt in the NBS 889 tungsten carbide reference material lie within 2.5% of the certified value. This shows that an accuracy of at least ±2.5% can be achieved relatively easily in a commercial laboratory. The narrower range of ±1.6% indicated by the certified uncertainty of the NBS 889 reference material could be achieved but at the expense of speed and sample throughput. More aliquots of each sample would have had to be dissolved and better instrumental precision would have had to be attained. This was not considered practical in laboratories where time and money were at a premium, and the clients indicated that they were satisfied with the accuracy

and precision obtained. Therefore, the analyses were repeated only when the measured cobalt concentration for the NBS 889 reference material fell outside the range 9.26 g/ 100 g to 9.74 g/ 100 g.

The cobalt content of the tungsten carbide samples analysed ranged from about 4 g/ 100 g to about 15 g/ 100 g. If the sample were diluted by a factor of 2000 times during the preparation step, solution concentration ranges of between 20 and 75 mg/ ℓ would be obtained. The measurement range would lie towards the centroid of the calibration curve if the instrument were calibrated from 0 to 100 mg/ ℓ.

Under the analytical conditions employed for cobalt (dilution factor = 2000), a 0.5 mg/ ℓ measurement inaccuracy would lead to a deviation of 0.1 g/ 100 g in the final results. In practice, using the quality control measures described in Section 6.4, a measurement inaccuracy of not more than ±0.5 mg/ ℓ was achieved (see Table 6.5) even though the presence of hydrogen peroxide in the solution tended to produce fine bubbles during nebulization (leading to a decrease in precision). At the cobalt levels measured, this resulted in a relative deviation from the true value of ±2%. Other factors also combine to increase the final uncertainty level.

To maintain analytical credibility, it is recommended that a certified reference material be analysed with every batch of commercial samples. This may become costly when a large number of samples are analysed. The problem can be overcome by using a secondary reference material which has been analysed repeatedly against a certified reference material.

The results obtained using this method are satisfactory for a laboratory making routine measurements of cobalt in tungsten carbide. There is no evidence that the hydrogen peroxide/ aqua regia acid dissolution is not effective for cobalt in tungsten carbide.