CHAPTER 10

MEASUREMENT OF CHROMIUM

10.1 WAVELENGTHS SELECTED

Several chromium emission lines are recommended in the Jobin Yvon software (version 5): the Cr emission lines at 205.559 nm, 266.602 nm, 283.563 nm and 357.869 nm. Thompson & Walsh (1983) recommend the line at 267.654 nm for the analysis of chromium in soil. Each of these lines was investigated and only the 357.869 nm emission line, also recommended by Piippanen et al (1996a), gave consistently good results, as will be shown later. However, this line has cobalt emission lines at 357.890 nm and 357.903 nm (Harrison, 1969) but matrix matching could be applied to correct the problem. No interference from tungsten could be observed. All the other lines were found to have interferences from tungsten emission lines. Since the tungsten concentration in the sample solutions was very high compared to the chromium concentration (see Table 10.2), matrix matching with tungsten was not an option.

10.2 MATRIX EFFECTS AND INTERFERENCES

The potential interferences at each line were researched in the literature (Boumans, 1984; Harrison, 1969). Table 10.1 gives a summary of the information obtained.

Table 10.1: Summary of potential interferences in chromium analysis by ICP-OES

Cr emission line	Interferent	
	Element	Emission line
205.559 nm	W	205.602 nm
266.602 nm	W	266.564 nm, 266.577 nm, 266.608 nm
267.654 nm	W	267.631 nm, 267.641 nm
283.563 nm	W	283.564 nm
357.869 nm	Co	357.890 nm, 357.903 nm

The emission profiles of a solution of 10 mg/ ℓ chromium in 0.5 M hydrochloric acid and that of a 10 mg/ ℓ chromium solution in 1000 mg/ ℓ tungsten were compared at each wavelength. The effect of cobalt at 357.869 nm was also investigated. Some of the effects are documented in Figure 10.1.

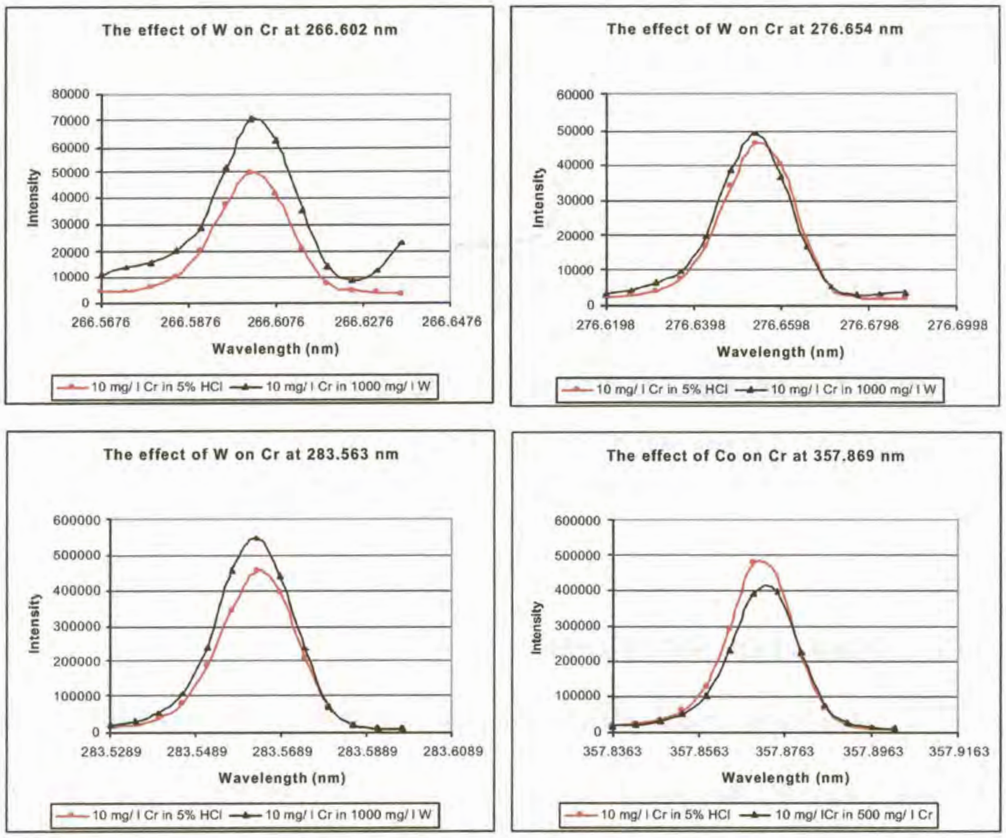

Figure 10.1: *Effect of W and Co at various Cr emission lines (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)*

From Figure 10.1 it can be seen that the tungsten interference at all the Cr II lines precludes their use for the quantitative measurement of chromium.

Although no cobalt emission lines could be found in the literature near 276.654 nm, a cobalt interference was observed near this chromium emission line, as is shown in Figure 10.2.

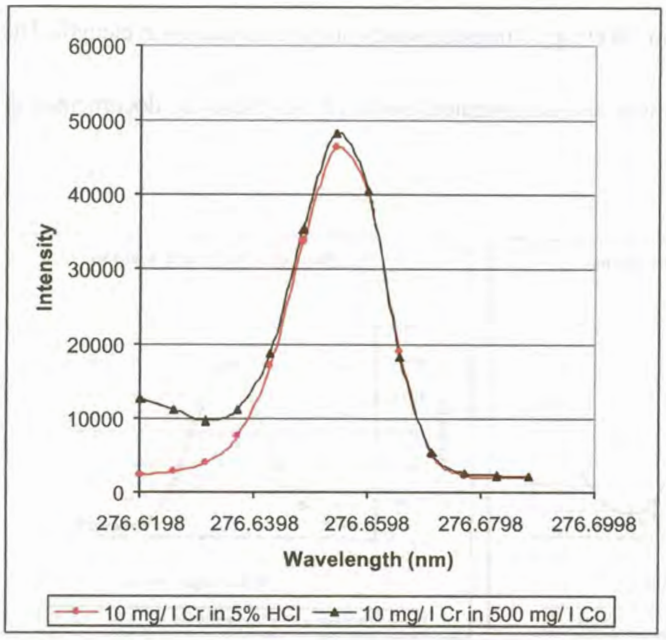

Figure 10.2: Effect of Co on Cr at 276.654 nm (JY-24 ICP-OES), where 5% HCl refers to a 0.5 M solution (5% v/v dilution from concentrated HCl)

10.3 CALIBRATION SOLUTIONS

The 357.869 nm chromium emission line was selected as the analytical line. As can be seen from Sections 10.1 and 10.2 the calibration and quality control solutions needed to be matrix matched with respect to cobalt. Since the chromium levels in the commercial samples rarely exceeded 0.07 g/ 100 g, a sample dilution factor of 200 was found to be appropriate. This dilution would result in cobalt concentrations in the solution of 250 to 750 mg/ ℓ.

Table 10.2 gives a summary of a typical composition of the analytical solution with respect to cobalt, tungsten and chromium.

Table 10.2: Summary of solution for the analysis of chromium in tungsten carbide

Analyte	Chromium
Mass dissolved	0.5 g
Final volume	100 ml
Dilution factor	200
Concentration chromium in solution	0 – 15 mg/ ℓ
Concentration cobalt in solution	50 – 750 mg/ ℓ
Concentration tungsten in solution	~ 4250 mg/ ℓ
Matrix matching of calibration solutions?	Yes , wrt to cobalt

Table 10.3 gives an example of a typical scheme for the preparation of a series of chromium calibration solutions, matrix matched with cobalt, for samples which contain 0.01 to 0.07 g/ 100 g chromium and about 10 g/ 100 g cobalt at a dilution factor of 200. The chromium was obtained from Merck Chemicals, as a 1000 mg/ ℓ certified solution. The cobalt solution was also obtained from Merck Chemicals.

Table 10.3: Summary of the preparation of a series of chromium calibration solutions: sample chromium content 0.01- 0.07 g/ 100 g, cobalt content 10 g/ 100 g. Sample dilution 0.5g /100 ml

Cr concentration required (mg/ ℓ)	Concentration of Cr stock solution (mg/ ℓ)	Volume of Cr stock solution (ml)	*Volume of 1000 mg/ ℓ Co (ml)	Volume of 32% HCl (ml)	Final volume (ml)
0	-	-	50.00	5	100.00
1	25	4.00	50.00	5	100.00
5	1000	0.50	50.00	5	100.00
25	1000	2.50	50.00	5	100.00

* Matrix matched to the cobalt concentration in the sample solutions, in this case 500 mg/ ℓ

A four point calibration of the ICP-OES was performed. A typical calibration curve at 357.869 nm, with a coefficient of correlation (r^2) of 0.99998, can be seen in Appendix 4, Figure A9. The limit of detection, calculated from this data according to the principles of Miller & Miller (1993), was 0.2 mg/ ℓ and the limit of quantification 0.6 mg/ ℓ.

The above method uses relatively large volumes of high purity cobalt solutions. To avoid this problem, the instrument was calibrated with chromium solutions in 0.5 M hydrochloric acid. One solution, with a chromium concentration which matched the sample concentration, was made up and used as a QC reference solution during the measurement run.

Table 10.4 gives a summary of a typical scheme for the preparation of calibration solutions in hydrochloric acid and a quality control reference solution, matrix matched with cobalt.

Table 10.4: Summary of the alternative preparation of a series of chromium calibration solutions: sample chromium content 0.1 g/ 100 g, cobalt content 10 g/ 100 g. Sample solution 0.5g /100 ml

Cr concentration required (mg/ ℓ)	Concentration of Cr stock solution (mg/ ℓ)	Volume of Cr stock solution (ml)	*Volume of 1000 mg/ ℓ Co (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
25	1000	2.50	-	5	100.00
#5	1000	0.50	50.00	5	100.00

* Matrix matched to the cobalt concentration in the sample solutions, in this case 500 mg/ ℓ
# Quality control solution (QC)

Because the calibration solutions had contained no cobalt, the measurement of the 5 mg/ ℓ QC solution gave a reading of 4.9 mg/ ℓ. The sample measurements were multiplied by a correction factor (prepared QC concentration/ measured QC concentration) to calculate the actual chromium concentration in the solutions.

10.4 REFERENCE MATERIALS AND QUALITY CONTROL

Unfortunately, no tungsten carbide certified reference material containing chromium could be obtained. The accuracy of the analysis was checked by adding known concentrations of chromium to sample solutions containing no chromium. One of the samples analysed had also been analysed by two other laboratories by XRF and the results could thus be compared.

Two samples of tungsten carbide-cobalt which contained no chromium were dissolved by the hydrogen peroxide/ aqua regia method. Portions of each solution were spiked with chromium to give a concentration of 1 mg/ ℓ. The ICP-OES was calibrated at 357.869 nm with a series of chromium solutions, as in Table 10.4. The spiked solutions were then measured at this wavelength. The readings obtained were within 5% of the prepared concentration (0.95 to 1.05 mg/ ℓ). When no matrix matching of the calibration solutions was done, the measurements of the spiked solutions were about 7 % lower than expected.

A sample of tungsten carbide was received for analysis which had already been analysed by XRF at two independent laboratories. Triplicate aliquots of this sample were dissolved by the hydrogen peroxide/ aqua regia method to give a dilution factor of 200. The solutions were measured at 357.869 nm after calibration with a series of chromium solutions in hydrochloric acid. A QC solution of 0.5 mg/ ℓ chromium in 250 mg/ ℓ cobalt was measured to obtain a correction factor for the calculation of the actual concentration of chromium in the solution. An average chromium concentration of 0.01 g/ 100 g for this sample was reported. The other laboratories had obtained values of 0.011 and 0.012 g/ 100 g, respectively. According to the calibration data in Section 10.3 the limit of quantification is 0.6 mg/ ℓ. Since the concentration of chromium in the solution was about 0.5 mg/ ℓ, very accurate results could not be obtained and no confidence limits were reported.

In order to demonstrate the effect of selecting an inappropriate analytical wavelength, one of the samples was analysed at three different chromium emission lines. Two of these wavelengths were shown to be subject to tungsten emission interferences (Section10.2). The results are given in Table 10.5. The sample was known to contain 0.01 g/ 100 g.

Table 10.5: Effect of different analytical wavelengths on the calculated chromium concentration

Analytical wavelength (nm)	Calculated chromium concentration (g/ 100 g)
205.559	<0.04
283.563	0.08
357.869	0.01

When a solution of tungsten carbide which contained no chromium was measured at 283.563 nm, a reading of 3.563 mg/ ℓ was obtained. The same solution measured at 357.869 nm gave a reading of -0.005 mg/ ℓ. This shows that false positive results for chromium and incorrect concentrations may be obtained if care is not taken.

As with the analyses of other elements in a tungsten carbide matrix, at least two aliquots of each sample were dissolved and replicate measurements made on some of the solutions. Quality control solutions of known concentration were measured after at least every three sample solutions. The measurements at the beginning of the analytical run were within 5% of the measurements of the same solutions at the end of the run, indicating good instrumental stability.

10.5 DISCUSSION AND CONCLUSIONS

No chromium could be detected in about half of the commercial samples analysed. A chromium detection limit (LOD) of 0.004 g/ 100 g in the sample was calculated directly from the calibration data in Section 10.3. The dilution factor was 200.

Two of the samples contained chromium in concentrations of about 0.01 g/ 100 g, which at the minimum dilution possible, fell between the LOD and the LOQ.

In the remaining samples, the chromium concentration was found to be between 0.14 and 0.22 g/ 100 g. These concentrations, after sample preparation, fell into the calibration range used. The cobalt concentrations in the reference solutions were adjusted to match those of the different sample solutions.

Table 10.5 illustrates the point made in previous chapters about the advisability of using at least two different analytical wavelengths for each element. In the case of chromium, only one suitable wavelength was available. Therefore, the matrix of the sample solution should be well characterised. The measurement of chromium in samples which contain unusual elements should be re-evaluated, ideally by the method of standard additions.

Since one of the samples had been analysed by two other laboratories by XRF and the ICP-OES results agreed closely with the XRF results, it can be concluded that there is no difficulty in dissolving chromium in tungsten carbide by the hydrogen peroxide/ aqua regia method. The measurement method has also been shown to produce accurate results.