CHAPTER 5

INSTRUMENTATION

5.1 INTRODUCTION

Detailed information on ICP-OES systems can be obtained from the works of Moore (1989), Boss & Fredeen (1999), Thompson et al (1983), Tissue (1996) and Townshend et al (1995). A brief description from these sources follows.

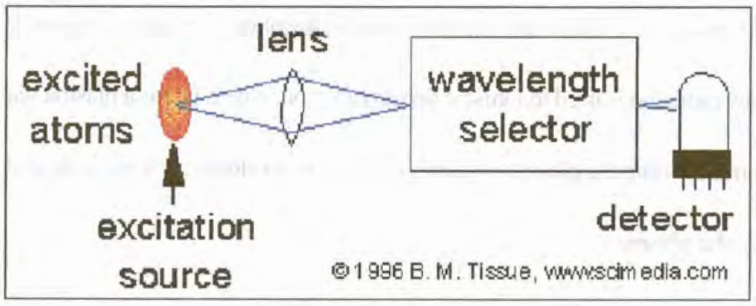
Inductively coupled plasma analysis usually involves the introduction, in liquid form, of the elements to be analysed in an argon plasma, induced by a high-frequency field and realizing temperatures in the region of 8 000 K. With the aid of a stream of argon gas, a nebulizer transforms the liquid into an aerosol. Separation of the large droplets is achieved in a spray chamber. The aerosol/ argon mixture passes through an injector tube into the plasma. There the aerosol is atomised and excited.

When the atoms of an element are excited, their electrons change energy levels by absorbing energy, and light with a characteristic wavelength is emitted when the electrons return to their ground state. The energy required to excite the atoms or ions is supplied by a radio frequency generator. High frequency radiation is used to ionise a stream of argon, which forms a plasma via an induction coil. The sample within the plasma is mostly reduced to an atomic or ionic state and the atoms are excited by the plasma.

Discrimination between these wavelengths is performed by a spectrometer which can take the form of a monochromator or polychromator. The beam of light is focussed onto the primary slit of the spectrometer by a convergent lens and then reaches an interferometric (holographic) diffraction grating. When light strikes the grating, which has closely spaced grooves etched into its surface, the light is diffracted at an angle that is dependent on the wavelength of the light and the line density of the grating.

A photomultiplier tube or solid state detector behind the exit slit receives the radiation and transforms it into electrical signals which are captured by the data processing system. As each angular position of the grating corresponds to a well-defined wavelength, each beam of light passing though the exit slit of the monochromator is characteristic of the elements analysed (qualitative analysis). The intensity of the light beam falling onto the detector is measured and is proportional to the concentration of each element in the sample aerosol. A calibration curve for each element can be drawn up by the data processing system and the concentration of the elements may be determined (quantitative analysis).

Figure 5.1 (Tissue, 1996) shows a simplified representation of an atomic emission system. Detailed descriptions of each component part of the ICP-OES system follow in this chapter.



©1996 B. M. Tissue, www.scimedia.com

Figure 5.1 : Schematic diagram of an atomic emission system (Tissue, 1996)

5.2 INSTRUMENTATION /THEORY

The experimental work was performed using a Jobin Yvon JY-24 sequential ICP-OES system, shown in Figure 5.2. The JY-24 is equipped with a 0.64 m Czerny-Turner monochromator, a direct drive 2400 lines per mm grating and a 40.68 MHz generator.

Figure 5.2: The Jobin Yvon inductively coupled plasma-optical emission spectrometer (Jobin Yvon Emission Instruments S.A.)

The sample introduction system is thermoregulated and includes an argon humidifier. A separate attachment for argon sheath gas is supplied. The use of the sheath gas attachment allows a tangential stream of argon to reduce contact of the sample aerosol with the injector tube. According to Jobin Yvon Emission Instruments S.A, sheath gas prevents crystallization at the top of the inner torch tube when samples with a high salt content are analysed, and it also helps to reduce memory effects. With the JY-24, the sheath gas flow rate is automatically adjusted when alkali elements are analysed, so that the plasma is optimised for the best limits of detection.

A Meinhard concentric nebulizer with a 3 ml/ minute flow rate and a Schott double pass glass spray chamber were used. All the work was carried out using a demountable torch.

5.2.1 The Monochromator

Accoding to Moore (1989), sequential instruments are designed to move sequentially from one wavelength to the next during the measuring sequence. It therefore measures the elements in the sample one after the other. Faster results are obtained with simultaneous (measuring all the elements at the same time) instruments. The main reason that sequential instruments are used is to save costs but there is also increased flexibility. An almost unlimited range of analytical lines can be used.

In sequential instruments, a monochromator enables a specific spectral band to be selected. The emission spectrum of an ICP plasma is composed primarily of spectral lines over a continuous background and is very complex. Each element emits radiation at characteristic wavelengths and so the precision of the analytical results depends on the separation of the spectral lines.

The JY-24 utilises a 0.64 m focal length monochromator with a plane interferometric (holographic) grating. A wavelength drive is used with a computer-controlled stepper motor. A schematic representation of the Czerny-Turner mounting is presented in Figure 5.3 (Thompson et al, 1983). The grating is rotated and the spectrum is moved across the exit slit.

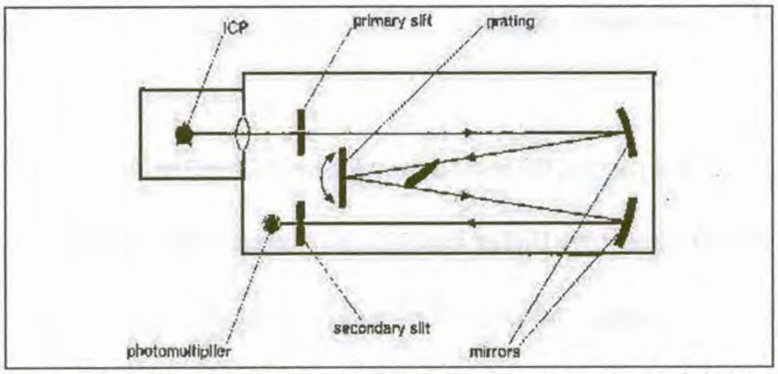


Figure 5.3: Schematic of a Czerny-Turner mounting (Thompson et al, 1983)

The JY-24 also includes a second, smaller monochromator, a reference monochromator. When using an internal standard in the sample solution, the emission for this element is measured by the reference monochromator at the same time as the primary monochromator measures the element of interest at the chosen wavelength. In this manner the operator can compensate for small fluctuations in the measurement system and produce more accurate results. If the primary monochromator were used to measure the emission of the internal standard as well as that of the sample, the monochromator would have to move from one wavelength to the other during the procedure. This means that the measurements would not be simultaneous, but sequential, and true internal standardization would not have taken place. Internal standards, such as yttrium, are normally used to correct for small system instabilities (e.g. power or nebulizer pressure fluctuations). They would not correct for systemic effects, such as spectral interferences.

Diffraction gratings are dispersive optical components with grooves or lines parallel to each other. The JY-24 includes an interferometric (holographic) grating, on which the lines are produced by the interaction of an interference pattern with a photosensitive layer (ruled gratings are mechanically produced by a ruling engine or laser). Interferometric gratings are considered superior to ruled gratings as they have a very high stray light rejection and the lines are better distributed across the surface of the substrate. Because interferometric gratings have negligible groove errors, very high resolution is possible.

The higher the number of lines per mm, the better the resolution which can be obtained. The JY-24 has a grating with 2400 lines/ mm. Higher resolution is obtained with instruments using a 3600 lines/mm grating but sodium, lithium and potassium cannot be measured due to a decreased wavelength measurement range (Jobin Yvon Emission Instruments S.A.).

A schematic diagram of how the diffraction grating separates two wavelengths of light is shown in Figure 5.4 (Boss & Fredeen, 1999).

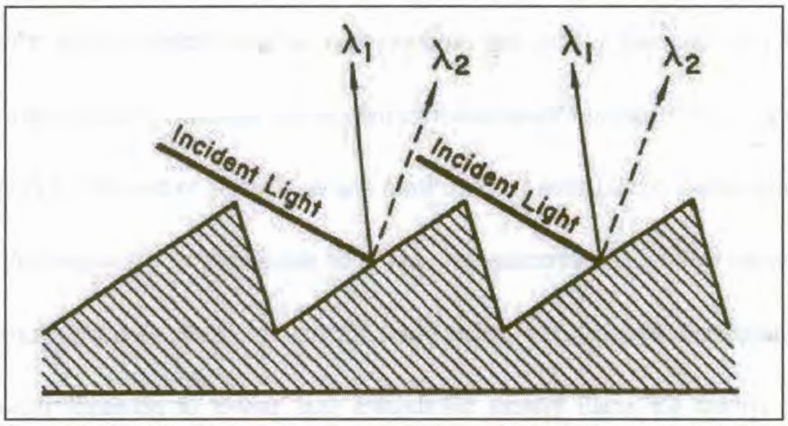


Figure 5.4: Diffraction grating separating two wavelengths of light (Boss & Fredeen, 1999)

5.2.2 The Generator

The 40.68 MHz radio frequency generator of the JY-24 ICP-OES has a system of anode lines tuned to a quarter wavelength controlling frequency. It is equipped with a voltage stabilizer and a reflected power controller. The power can be set at two pre-selected levels (1 kW or 1.1 kW) or may be varied continuously up to a maximum incident power of 2300 VA. The power is transmitted to the plasma torch via a water-cooled 3-turn induction coil. The power setting used for the work described here was 1 kW. The generator also has an automatic plasma ignition system and protection against leaks and outside radio frequencies.

5.2.3 The Torch

The demountable ICP torch consists of two concentric quartz tubes (connected to the argon source) which surround the central injector tube. The injector tube is connected to the nebulizer via the sheath gas system and is constructed of alumina, quartz or sapphire. A 3 mm alumina tube was used in all the experimental work. When solutions of tungsten carbide are analysed by ICP-OES, a black deposit builds up on the quartz torch. The deposit cannot be removed and eventually makes the quartz brittle, causing it to flake off the edges. Alumina was found to remain smooth in spite of the deposit. A schematic representation of the demountable torch is shown in Figure 5.5.

One argon inlet on the torch supplies cooling gas and supplies the plasma itself, while another supplies auxiliary (argon) gas, required during the analysis of samples containing organic solvents. There is also an inlet from the nebulizer and a sheath gas supply. The latter two are used for the formation, transport and injection of the sample aerosol into the heart of the plasma. An argon flow rate of 14 ℓ/ min was used for the cooling/ plasma generation supply. Argon flow rates for the sheath gas and nebulizer were set at 0.2 ℓ/ min and 0.3 ℓ/ min, respectively. The auxiliary gas supply was not required.

As mentioned above, the analysis of tungsten carbide samples was found to cause a black deposit to build up on the quartz outer torch tube. This outer tube is shown in Figure 5.5. When other types of sample were analysed on the same instrument, the demountable system allowed the replacement of only the outer torch tube. It also contributes to considerable cost savings when the tube is to be replaced.

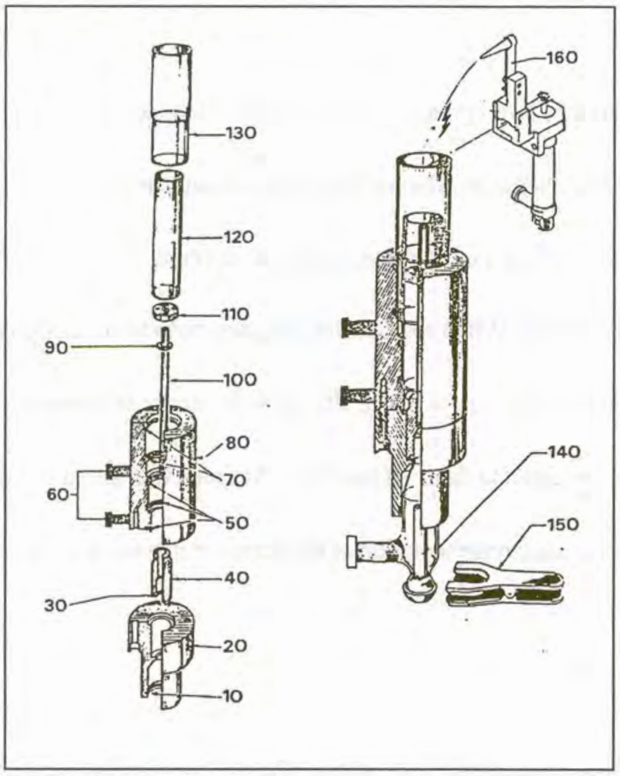


Figure 5.5 : Schematic of the Jobin Yvon demountable torch and holder, (Jobin Yvon Emission Instruments, S.A.) where:
130 is the outer torch tube with a ground fitting
120 is the inner torch tube
100 is the alumina injector tube, which is centred in the torch by a spacer (110)
60 is the argon inlet, the upper coupling supplies the plasma while the lower coupling supplies the auxiliary gas
20, 40 and 80 are supports for the sheath gas device, the injector and the torch, respectively
10, 30, 50, 70 and 90 are o-rings which ensure a leak-free system
140 is the sheath gas device
160 is the plasma ignitor
150 is the clamp connecting the spray chamber to the sheath gas device

5.2.4 The Plasma

The following description of an ICP plasma was found in the works of Moore (1989) and Thompson et al (1983). A plasma consists of partially ionised atoms or molecules. Radio frequency currents in the induction coil create oscillating magnetic fields whose force lines are orientated axially to the inside of the quartz tube. Induced currents (Foucault currents) are formed. This works on the same principle as the secondary winding of a transformer in short circuit. The electrons are accelerated at each half-period, since the induced magnetic fields vary in both intensity and direction. Heating occurs because of the acceleration and resistance of the argon electrons to the movement (changes in kinetic energy).

Initially, the electrons or ions must be seeded in order to create the plasma. After this, the plasma is self-perpetuating in the same way as a transformer (with the induction coil as the primary winding and the plasma as the secondary winding). The plasma may reach temperatures in the order of 6 000 to 10 000 K. To prevent the quartz tube from melting, a flow of cooling argon gas isolates the plasma from the quartz tube. The dissociation and ionization of the sample aerosol will be more efficient if the particles pass through the centre of the plasma (7 000 to 10 000 K). A representation of an inductively coupled plasma is presented in Figure 5.6. (Tissue, 1996).

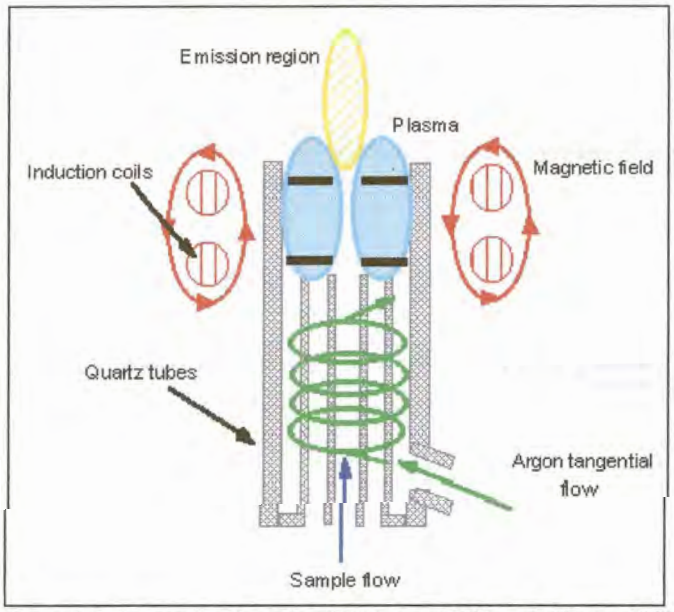


Figure 5.6: Representation of a plasma in an ICP torch (Tissue, 1996)

5.2.5 The sample introduction system

The sample, in liquid solution form, is pumped to the nebulizer via a peristaltic pump. Peristaltic pumps use a series of rollers that push the sample solution through the tubing (peristalsis). The pump itself does not come into contact with the solution and thus contamination from the pump is not a consideration. Pump tubing of inner diameter 0.030 cm was used. The pump speed was set at 30 ml/ min and this system was found to deliver the sample solution to the nebulizer at a rate of 2.5 ml/ min.

The nebulizer, in this case a glass Meinhard concentric nebulizer with a flow of 3 ml/ min, converts the liquid into an aerosol that can be transported to the plasma (Boss & Fredeen, 1999). The nebulization process is one of the critical processes in ICP analysis. Because only small droplets are useful in ICP analysis, the ability of the nebulizer to produce small droplets for a wide variety of samples largely determines the effectiveness of the nebulizer. Pneumatic nebulizers use high-speed gas flows to create the aerosol. The solution is forced through a capillary tube to a low pressure region created by a gas flowing rapidly past the end of the capillary. The low pressure and the high-speed gas combine to break up the solution into an aerosol. The construction of a Meinhard concentric nebulizer is shown in Figure 5.7. (Boss & Fredeen, 1999).

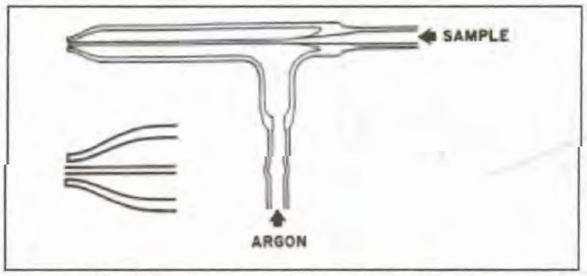


Figure 5.7: A Meinhard nebulizer used for ICP, constructed of borosilicate glass (Boss & Fredeen, 1999)

Because ICP nebulizers require lower sample carrier flow than atomic absorption nebulizers, the liquid and gas orifices are smaller. The concentric pneumatic nebulizers give excellent sensitivity and stability but are more subject to clogging, especially with solutions containing high concentrations of dissolved solids. The JY-24 is equipped with an argon humidifier, which produces moist argon and decreases the possibility of crystallization in the nebulizer. It also helps to keep the torch clean. The humidifier is, basically, a vessel filled with water though which the argon flows prior to reaching the nebulizer.

The aerosol passes into the spray chamber, which is designed to separate large drops from the aerosol and direct them to the drain. According to Moore (1989), spray chambers also smooth out pulses that occur during nebulization due to pumping of the solution. ICP spray chambers generally separate out droplets larger than 10 μm. This amounts to 95 to 99% of the sample being discarded. A Scott double pass spray chamber, similar to that shown in Figure 5.8 (Boss & Fredeen, 1999), was used in the experimental work.

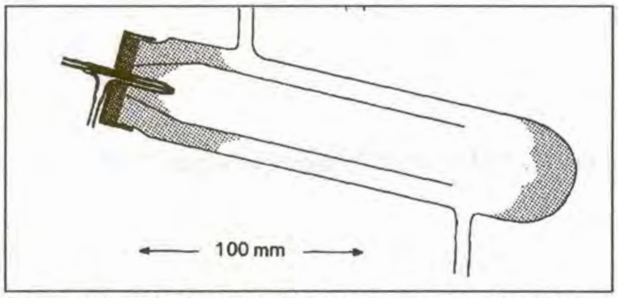


Figure 5.8: The Scott double pass spray chamber (Boss & Fredeen, 1999). The nebulizer is shown entering the spray chamber at the left.

From the spray chamber, the aerosol passes though the sheath gas device and is injected into the plasma through an injector tube. The injector tube is shown in Figure 5.5 and is held centrally in the inner torch tube by a specially designed spacer. A 3 mm alumina injector tube is used, since alumina was found to withstand continuous use better than quartz, remaining smooth even when a deposit forms on the tip. The alumina injector tube could be used over a period of several months before it had to be replaced. However, dissolved solids may cause clogging in the injector tube. To overcome this problem, the JY-24 has a sheath gas system. The sheath gas device produces a stream of argon which perfectly 'sheaths' the sample and prevents the aerosol from coming into contact with the sides of the tube. This reduces memory effects from the tube and prevents clogging.

For sodium only two lines are generally recommended, 588.995 nm and 589.59 nm, and for potassium only the 766.49 nm line is used. Since these elements also behave differently from other elements, it is important that conditions for these elements are optimised. Sodium and potassium are measured using atom lines and they have lower ionisation potentials than other elements. The best emission intensities are obtained higher in the ICP plasma, where the degree of ionisation is lower (Thompson and Walsh, 1983). Therefore, when alkali elements are analysed, the sheath gas is automatically adjusted to give optimum sensitivity for these elements (Jobin Yvon Emission Instruments S.A.).

The sample introduction system of the JY-24 ICP-OES is shown in Figure 5.9.

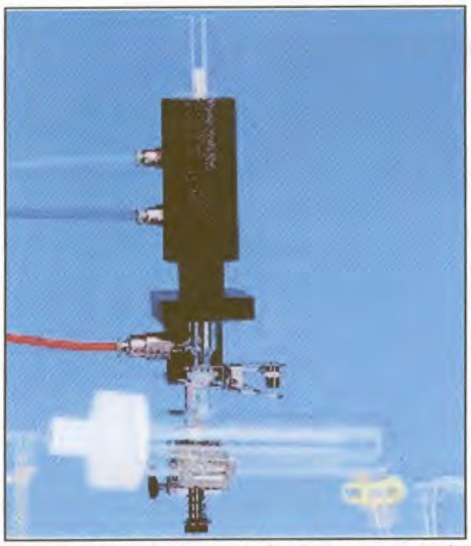


Figure 5.9: Sample introduction system (Jobin Yvon Emission Instruments S.A).
The spray chamber with a sheath gas device and the torch in its support are shown.
The nebulizer can be seen in the spray chamber to the left.

5.2.6 The Detector

Once the proper emission line has been isolated by the spectrometer, the detector is used to measure the intensity of the emission line. According to Boss & Fredeen (1999), the most common is still the photomultiplier tube (PMT), which is also used in the JY-24. The PMT is a vacuum tube that contains a photosensitive material, the photocathode. The photocathode ejects electrons when it is struck by photons of light. These ejected electrons are accelerated towards a dynode which ejects two to five secondary electrons for every electron that strikes its surface. The secondary electrons strike another dynode and a multiplicative effect is caused. Typical PMTs contain 9 to 16 dynode stages. The final step is the collection of the secondary electrons at the last dynode by the anode. A typical PMT is shown in Figure 5.10 (Boss & Fredeen, 1999). The electrical current measured at the anode is used as a relative measure of the intensity of the radiation at the PMT. The PMT can be used to amplify very weak signals and its range of response can be extended over nine orders of magnitude in light intensity.

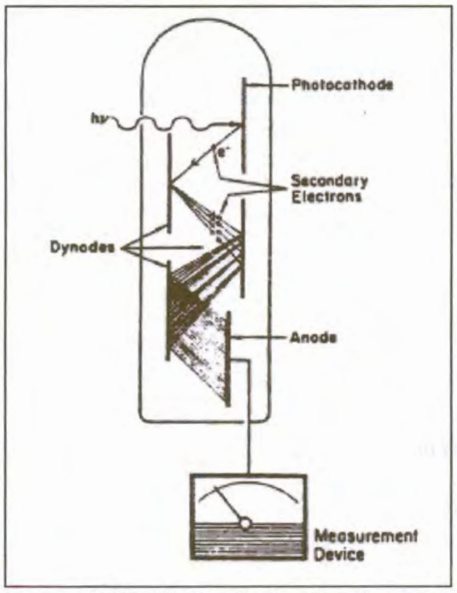


Figure 5.10: Photocathode, dynode and anode layout of a photomultiplier tube (Boss & Fredeen, 1999)

5.3 INSTRUMENT CONDITIONS

The radio frequency on the JY-24 ICP-OES is 40.68 MHz. The monochromator has a focal length of 0.64 m and the grating is grooved at 2400 lines/ mm. The following conditions were maintained for all the sample measurements:

RF power:	1000W
Reflected power:	<1W
Plasma argon flow:	14 ℓ/ min
Nebulizer argon flow:	0.3 ℓ/ min
Sheathing argon flow:	0.2 ℓ/ min

The JY-24 is capable of measuring a chosen reference line before every analysis. This is to check that the monochromator is still properly aligned to measure the correct wavelength. The carbon line at 193.026 nm was chosen because it is possible for the instrument to measure atmospheric carbon dioxide (and so no special sample needs to be introduced though the nebulizer).

The entrance slit of the monochromator was set at 20 motor steps and the exit slit at 25 steps. As each motor step corresponds to 0.001 nm, the slits are effectively 0.020 nm and 0.025 nm wide. This is the recommended setting for measurements in the concentration range 0.5 to 50 mg/ ℓ for the JY-24 instrument. The resolution of the monochromator is defined by the width of the slit used. The narrower the slit, the better the sensitivity and resolution but a higher integration time when measuring is also required (Jobin Yvon Emission Instruments, S.A.).

For the data acquisition (measurement) phase of the analysis, the 'Gaussian' mode was selected. The software scans around the theoretical position of the peak and determines a gaussian curve corresponding to these points. This mode can compensate for small variations in the peak position. The integration time for each point is short (0.5 s) because a relatively large number of data points were chosen. For the measurement, 9 data points were selected while the calculation of the gaussian curve was based on 5 points. This setting gives the best compromise between measurement speed and precision. When 11 measurement points and 7 calculation points are selected, for example, the measurement would be slower but precise. A choice of 7 measurement points and 5 calculation points would result in a faster but less precise measurement.

5.4 REAGENTS AND REFERENCE MATERIALS

Certified stock reference solutions of tungsten, cobalt, tantalum, titanium, vanadium and chromium were obtained as 1000 mg/ ℓ solutions from Merck Chemicals. The cobalt solution used to matrix match the calibration solutions was prepared from the dissolution of pure cobalt sponge (BDH) in dilute hydrochloric acid.

The stock solutions were diluted with 8.2 MΩ.cm deionised water and analytical reagent (AR) grade hydrochloric acid.

The hydrogen peroxide used for the dissolution step was BDH analytical grade and the tartaric acid Merck AR grade.

5.5 STATISTICAL TREATMENT

Several statistical methods were used during the evaluation of the results and were applied mainly to assess the precision, accuracy and confidence limits. The work of Miller & Miller (1993) was used as a guide. These methods were also used to compare the results of two different sets of measurements. Only statistical methods which were used in the evaluation of experimental results are discussed, and this section is not intended as an exhaustive guide to statistics.

The mean was calculated according to the formula:

$$\bar{x} = \frac{\sum_i x_i}{n} \qquad (5.1)$$

in order to report a single representative value from a series of measurements.

The standard deviation, s,

$$s = \left\{ \frac{\sum_i \left(x_i - \bar{x}\right)^2}{n-1} \right\}^{\frac{1}{2}} \qquad (5.2)$$

gives a measure of the spread of the results around the mean value. The standard deviation is used in many calculations (e.g. confidence and tolerance intervals, significance tests, evaluation of proficiency studies). If the data tends towards a normal distribution, the standard deviation may be used to estimate the confidence limits of the mean. The rule of such distribution predicts that 95% of the measurements will fall within 2s of the mean, while 99% of the results will be within 3s of the mean.

The standard deviation is sometimes expressed as a percentage, i.e. $100s/\bar{x}$, and is called the relative standard deviation (RSD) or the coefficient of variation (CV). The RSD has the advantage of enabling the comparison of the spread of different sets of results with differing means.

The confidence limits of the mean are generally calculated from the formula

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \qquad (5.3)$$

which is especially appropriate for small sample sizes. In practice the t-values provided by statistical tables or by computer software are related to the number of degrees of freedom (usually given the symbols d.f. or the Greek letter ν) involved in the calculation. Confidence levels of 95% were employed throughout.

Rearrangement of equation 5.3 gives

$$t = |\ \bar{x} - \mu\ |\ \frac{\sqrt{n}}{s} \quad \text{or} \quad t = \frac{|\bar{x} - \mu|}{s/\sqrt{n}} \qquad (5.4)$$

and allows the comparison of the mean of an experiment with a reference value. The calculation is normally done in a 2-tailed form, since it is not known beforehand whether the mean will be higher or lower than the expected ('true') value. The t-tests were performed with the aid of Microsoft Excel spreadsheets.

The estimated standard deviation, s_{x0}, on the concentration values, x_0, can also be calculated to obtain a measure of the uncertainties involved. According to Miller and Miller (1993: 113) it can be shown that the optimum number of standards in a calibration curve is seven. In this study, four-point calibration curves were used, since the samples were analysed in a routine laboratory where the best quality results are balanced with turn-around time and cost reduction. The calculation of s_{x0} gives an estimate of the error in the measurement, but other effects, such as sampling, sample dissolution and dilution errors also affect the uncertainty. At least two aliquots of each sample were dissolved and analysed, mostly at two analytical lines, and equation 5.3 was used as an approximation of the combined measurement uncertainty. The recent international trend towards comprehensive uncertainty calculations would certainly require that a more complete estimate be produced.

The F-test, conveniently performed with the help of a Microsoft Excel spreadsheet, is used to compare the standard deviations of two samples, i.e. relating to the precision of the results. F is given by

$$F = \frac{S_1^2 / \sigma_1^2}{S_2^2 / \sigma_2^2} \tag{5.5}$$

The null hypothesis is that H_0: $\sigma_1^2 = \sigma_2^2$ thus the equation 5.5 becomes:

$F=s_1^2/s_2^2$, or s_2^2/s_1^2 (5.6)

with F always larger than 1. Values of F greater than the critical values (Microsoft Excel provides probability values directly) indicate that the ratio of the variances calculated is larger than would be expected at the confidence level in use (normally 95%), and hence that the null hypothesis of equal variances can be rejected.

The least squares principle was used for the regression statistics, where the least squares straight line is given by

$$y = bx + a \tag{5.7}$$

and

$$b = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sum_i (x_i - \bar{x})^2} = \frac{n\sum_i x_i y_i - \sum x_i \sum y_i}{n\sum_i x_i^2 - (\sum x_i)^2} \tag{5.8}$$

The correlation coefficient was calculated from the formula

$$r = \frac{\sum xy}{\sqrt{\sum x^2 . \sum y^2}} \tag{5.9}$$

but the coefficient of determination (r^2) was used throughout this text to estimate the linear fit to the data. The data was plotted and linearity confirmed by visual inspection.

The random error in x and y of the regression line: y = bx + a was found from

$$s_{y/x} = \left\{ \frac{\sum_i (y_i - \hat{y}_i)^2}{n-2} \right\}^{1/2} \tag{5.10}$$

The error of the slope was calculated from

$$s_b = \frac{s_{y/x}}{\left\{ \sum_i (x_i - \bar{x})^2 \right\}^{1/2}} \tag{5.11}$$

while the error in the intercept is given by

$$s_a = s_{y/x} \left\{ \frac{\sum_i x_i^2}{n \sum_i (x_i - \bar{x})^2} \right\}^{1/2} \tag{5.12}$$

The limit of detection (LOD) was calculated as the analyte concentration giving a signal equal to the blank signal, y_B, plus three standard deviations of the blank, s_B:

$$\mathrm{LOD} = y_B + 3s_B \tag{5.13}$$